

AN INVESTIGATION OF SOME  
MAGNETICALLY ANOMALOUS COBALT(II)  
COMPLEXES

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## INTRODUCTION

During the past sixty or seventy years, the field of coordination chemistry has grown from a small and limited area to what is presently the most active area of inorganic chemical research. Many different approaches have been used to investigate such properties as the stereochemistry and bonding of coordination compounds. One such approach, the measurement and interpretation of the magnetic properties of transition metal compounds, has been particularly successful in contributing to the development and understanding of coordination chemistry.

For many years the magnetic moment has been used as a reliable indication of structure, that is, whether a complex is octahedral, tetrahedral, or square planar, the spin and orbital angular momenta contributions differing in many instances with these three stereochemistries. Much of the present interest in cobalt(II) is due to the fact that its complexes are illustrative of a rather large spectrum of stereochemical and magnetic properties common to transition metal complexes. The great majority of the complexes of cobalt(II) are octahedral, exhibiting magnetic moments between 4.7 and 5.2 Bohr magnetons (B.M.) (23,26). The

magnitude of magnetic moments in this range is attributable to a spin contribution of three unpaired electrons and a rather large orbital contribution. The large orbital contribution arises from the fact that an octahedral field about the cobalt(II) ion splits the  ${}^4F$  free ion term state into three new levels,  ${}^4T_1$ ,  ${}^4T_2$ , and  ${}^4A_2$ , of which the ground level is  ${}^4T_1$  (42). The threefold orbital degeneracy in the ground level is responsible for a large contribution to the magnetic moment of the complex (38,41). Additional orbital contribution is attributed to mixing of spin states of higher energy with the ground state (38). Octahedral complexes as described above are said to be "high spin."

Not all octahedral cobalt(II) complexes are high spin, however. When the ligand field strength is large, the crystal field splitting of the  $d$  orbitals increases, and eventually spin pairing occurs. The ground state corresponding to the new electronic configuration is  ${}^2E$ , and the complex is said to be "low spin." A small number of cobalt(II) complexes are known which fit into this category, exhibiting magnetic moments in the vicinity of 1.8 to 2.2 B.M. (6,48).

In tetrahedral complexes the energy levels are inverted from the order of octahedral complexes and the ground state for cobalt(II) is  ${}^4A_2$ , an orbital singlet. Thus, the orbital contribution to the magnetic moment is much less

than in the case of the octahedral complexes, arising principally from the mixing in of spin states of higher energy, and the resulting range of magnetic moments for tetrahedral cobalt(II) complexes is 4.1 to 4.5 B.M. (30, 35,36,38). Low-spin tetrahedral cobalt(II) complexes are not known.

Most square planar cobalt(II) complexes are of the low-spin variety, exhibiting magnetic moments in the vicinity of 2.1 to 2.9 B.M. (6,38,48). Only a few complexes of cobalt(II) known to be square planar are high spin; these exhibit magnetic moments between 4.8 and 5.2 B.M. (14,15,17). Ranges such as those listed above, however, are not strict, and exceptions are becoming more common as they are sought and as more complexes are prepared.

Transition metal complexes exhibiting unusual intermediate magnetic moments have uncovered several new areas for research. In several instances unusual magnetic behavior has led to the discovery that the complex in question was not a monomeric species, but a polymer, containing two, three, or more metal ions per formula weight (31,32). Nickel(II) complexes with various N-alkylsalicylaldimines and other ligands have been found to exist in square planar-tetrahedral equilibria, depending upon temperature, solvent, and size and position of substituent groups (2,20,46,47).

Existence of a planar-tetrahedral equilibrium of some cobalt(II) complexes in solution has been postulated (20, 40). Recently, however, increased interest has been focused upon an area in which the equilibrium apparently is not between structures but rather between electronic states (9,11,21,22,34,53,54,55).

Normal magnetic behavior, which follows the Curie-Weiss law, is described by the equation  $\chi = C/(T + \Theta)$ . This is represented graphically by plotting  $1/\chi$  versus  $T$ , in which case a straight line is obtained with a slope of  $1/C$  and intercept of  $\Theta/C$ . Cambi and Szego reported a series of closely related iron(III) complexes whose magnetic behavior is quite different from that usually followed by transition metal complexes (11). The plots of the iron(III) complexes in question are not straight lines. This anomalous Curie-Weiss behavior led to the suggestion that the complexes exist in a temperature-dependent equilibrium of high-spin and low-spin forms, shifting toward the low-spin form at low temperatures. The work by Cambi and Szego has been verified and extended recently to a series of nineteen N,N-disubstituted dithiocarbamates of iron(III). The anomalous magnetic moments were found to persist in chloroform and benzene solutions as well as in the solid state (21,55).

In 1956 Stoufer and Busch reported anomalous Curie-Weiss behavior for a cobalt(II) complex (53). A Boltzmann

distribution over high- and low-spin states was postulated. Research in this area has continued and the  $1/\chi$  versus  $T$  curves of nine anomalous cobalt(II) complexes have now been published (28,29,44,53,55). These are listed in Table 1 with their room-temperature magnetic moments.

In the various attempts to explain the anomalous magnetic behavior of these cobalt(II) complexes, several correlations have been attempted. It appears that a disproportionate number of anomalous complexes have tridentate ligands. A complex possessing two identical tridentate ligands such as 2,6-pyridinaldihydrazone has a unique axis of symmetry passing through the middle donor atoms of the tridentate ligands, giving rise to the possibility of Jahn-Teller-like distortion. Such an expansion along the  $z$  axis gives to the complex a structure approaching that of a square plane with the additional result that the magnetic moment is lowered to the 2.1 to 2.9 B.M. range. Research carried out along these lines by Ramirez showed some validity in the correlation (44). An anomalous complex was prepared by the use of a tetradentate ligand occupying the four planar positions and perchlorate ions, very weak donors, in the trans positions. Ramirez showed theoretically that whether the distortion is expansion or contraction along the  $z$  axis, the complex is more likely to be low spin than if there is no distortion at all.



TABLE 1

ROOM-TEMPERATURE MAGNETIC MOMENTS AND TEMPERATURE OF  $1/\chi$   
MAXIMA OF COBALT(II) COMPLEXES EXHIBITING ANOMALOUS  
CURIE-WEISS BEHAVIOR

Complex	$\mu_{\text{eff}}$	Temperature °K of $1/\chi$ maxima	Reference
$[\text{Co}(\text{PMI})_3](\text{BF}_4)_2$	4.31	125°	55
$[\text{Co}(\text{PBI})_2]\text{I}_2$	3.72	175°	55
$[\text{Co}(\text{BMI})_3]\text{I}_2$	2.91	205°	55
$[\text{Co}(\text{PdAdH})_2]\text{I}_2$	2.85	300°	55
$[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$	2.61	220°	34
$[\text{Co}(\text{DTPH})](\text{ClO}_4)_2$	2.36	285°	55
$[\text{Co}(\text{PvdH})_3]\text{Br}_2$	4.22	(no maximum)	27
$[\text{Co}(\text{GdH})_3]\text{Br}_2$	3.18	285°	27
$[\text{Co}(\text{PAPI})(\text{ClO}_4)_2]$	2.44	260°	44

Abbreviations: PMI, 2-pyridinalmethylimine; PBI, 2,6-pyridindialbis(benzylimine); BMI, biacetylbis(methylimine); PdAdH, 2,6-pyridindialdihydrazone; terpy, 2,2',2''-terpyridine; DTPH, 1,12-bis(2-pyridyl)-1,2,11,12-tetrakisaza-5,8-dithia- $\Delta^{2,10}$ -dodecadiene; PvdH, pyruvaldihydrazone; GdH, glyoxaldihydrazone; PAPI, bis(2-pyridinal)-o-phenylenediimine.



Further research in the area of anomalous cobalt(II) complexes has shown that ligand field strength and pi-bonding capabilities of the ligand are definite factors involved in causing the complex to exhibit an intermediate magnetic moment (27,28,29). It was shown that by decreasing steric repulsion and thus increasing the capability of pi-bonding, the ligand field strength for a particular type of coordinating group could be increased sufficiently to cause the cobalt(II) complex to exhibit anomalous Curie-Weiss behavior.

One argument for the lower magnetic moments of the anomalous compounds was based on the possibility of the complex actually being a mixture of high-spin cobalt(II) and diamagnetic cobalt(III) (55). The ease of oxidation of cobalt(II) complexes is well known (3,8,12,49). However, it has now been proved conclusively by Schmidt that the lower magnetic moments of the anomalous complexes are due to the presence of appreciable concentrations of the low-spin cobalt(II) species (50,51). Cobalt(III), being diamagnetic, does not exhibit an electron paramagnetic resonance (EPR) spectrum, and the EPR spectrum of high-spin cobalt(II) is extremely broad, with a g value of approximately 4. On the other hand, the narrowness of the EPR spectrum of low-spin cobalt(II), with a g value of approximately 2.1, makes

low-spin cobalt(II) especially well suited for EPR investigation (50,51).

Williams has shown that spin-orbit coupling affords an explanation of the existence of intermediate magnetic moments of cobalt(II) complexes near the cross-over point. But it does not resolve the problem of anomalous Curie-Weiss behavior in that the curves of  $1/\chi$  versus  $T$  calculated by including spin-orbit coupling do not contain maxima and/or minima as do the experimental curves. However, if in addition the ligand field strength is considered to be a function of temperature, the experimental  $1/\chi$  versus  $T$  curves could be reproduced (57).

Most of the complexes which show anomalous magnetic behavior are either perchlorate or iodide salts. From the statistical point of view, there should indeed be more anomalous complexes with perchlorate and iodide anions because these salts are usually the easiest to prepare because of their insolubility and therefore are considerably more prominent.

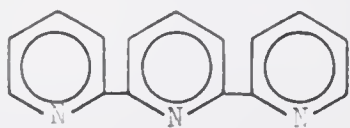
Hogg and Wilkins investigated the complexes of  $[\text{Co}(\text{terpyridine})_2]^{2+}$  with chloride, bromide, iodide, and perchlorate anions, finding their room-temperature magnetic moments decidedly different (34). They found the bromide monohydrate salt to exhibit anomalous Curie-Weiss behavior. The others were not investigated as a function of temperature

because their magnetic moments were thought to indicate normal high-spin or low-spin complexes.

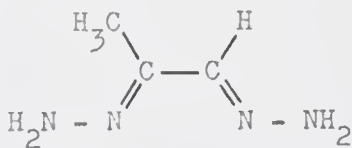
The research with which this dissertation is concerned deals with various effects of the solid state on the magnetic susceptibility of some complexes which are known to be near the cross-over point of cobalt(II), the cross-over point being defined as the point at which the  $^4T_1$  and  $^2E$  term states have the same energy. Since the magnetic behavior of anomalous cobalt(II) complexes has been measured on solid compounds, with the exception of two solution susceptibility measurements (54), there is the possibility that the anomalies observed might be caused by effects of the solid state. The purpose of this investigation, then, is threefold: (1) to determine whether the variation of the room-temperature magnetic moment as a function of the anion, as in the case of  $[\text{Co}(\text{terpyridine})_2]^{2+}$ , is an isolated case or a general phenomenon; (2) to determine how the anion effect is manifested as a function of temperature; and (3) to determine whether the unusual magnetic behavior observed is a result of an alteration of the stereochemistry of the complex in the solid state.

Three series of cobalt(II) complexes incorporating different ligands were chosen. Two of the ligands, terpyridine and pyruvaldihydrazone (Structures I and II), coordinate with cobalt(II) to produce anomalous salts (27,28,

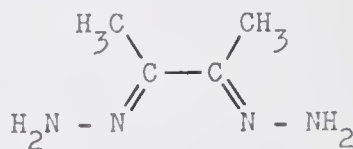
34). These salts are bis(terpyridine)cobalt(II) bromide monohydrate and tris(pyruvaldihydrazine)cobalt(II) bromide. The third ligand, biacetyldihydrazone (Structure III), is also known to produce a rather large crystal field splitting; the complex tris(biacetyldihydrazone)cobalt(II) iodide is reported to exhibit normal Curie-Weiss behavior with a Weiss constant of  $142^\circ$  (55). A series of anions was chosen with the intention of illustrating any effect of size and charge on the magnetic susceptibility. It was decided to employ X-ray diffractometry as a means of detecting crystalline alterations as a function of temperature. The entire investigation was centered, however, around proving a solid state anion effect by temperature-dependent measurements of the magnetic susceptibility by the Gouy method.



Structure I



Structure II



Structure III

## EXPERIMENTAL PROCEDURES

Many of the following preparations are similar in procedure. The differences in detail were found to be necessary modifications in the general method for the synthesis of the complexes. Therefore, each synthetic procedure is presented separately.

Pyruvaldihydrazone, PvdH.—Pyruvaldihydrazone was made by a method similar to that previously reported (28).

Tris(pyruvaldihydrazone)cobalt(II) bromide,  
[Co(PvdH)<sub>3</sub>]I<sub>2</sub>.—A solution of anhydrous cobalt(II) iodide (3.21 g, 0.0100 mole) in a minimum volume of warm absolute ethanol was added slowly with constant stirring to a solution of pyruvaldihydrazone (3.00 g, 0.0300 mole) in a minimum volume of warm absolute ethanol. The green microcrystalline product which formed immediately was collected on a sintered glass filter, washed with absolute ethanol, and dried over P<sub>4</sub>O<sub>10</sub> in vacuo. Yield, 85 per cent. Anal. for CoC<sub>9</sub>H<sub>24</sub>N<sub>12</sub>I<sub>2</sub>: C, 17.63; H, 3.83; N, 27.42. Found: C, 17.44; H, 3.86; N, 27.60.

Tris(pyruvaldihydrazone)cobalt(II) nitrate,  
[Co(PvdH)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.—This product was prepared by a method

analogous to that used for  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  using cobalt(II) nitrate hexahydrate. Yield of the dark green product was 90 per cent. Anal. calcd. for  $\text{CoC}_9\text{H}_{24}\text{N}_{14}\text{O}_6$ : C, 22.36; H, 5.01; N, 40.57. Found: C, 22.47; H, 4.99; N, 40.62.

Tris(pyruvaldihydrazone)cobalt(II) perchlorate,  $[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$ .—This green product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  using cobalt(II) perchlorate hexahydrate. Yield, 90 per cent. Anal. calcd. for  $\text{CoC}_9\text{H}_{24}\text{N}_{12}\text{Cl}_2\text{O}_8$ : C, 19.36; H, 4.33; N, 30.11. Found: C, 19.18; H, 4.32; N, 30.20.

Tris(pyruvaldihydrazone)cobalt(II) tetraphenylboron,  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$ .—A solution of anhydrous cobalt(II) chloride (0.65 g, 0.0050 mole) in warm absolute ethanol (25 ml) was added slowly with constant stirring to a solution of pyruvaldihydrazone (1.50 g, 0.015 mole) in warm absolute ethanol (25 ml). The solution darkened immediately, and after approximately one-half of the cobalt chloride solution was added, a solution of sodium tetraphenylboron (3.42 g, 0.0100 mole) in absolute ethanol (15 ml) was stirred in and then the remaining cobalt chloride solution was added. The dark green precipitate which formed was subsequently collected on a sintered glass filter, washed with hot absolute ethanol several times, then washed with a solution of 40 ml of water and 10 ml of ethanol, and dried



over  $P_4O_{10}$  in vacuo. Yield, 90 per cent. Anal. calcd. for  $CoC_{57}H_{64}N_{12}B$ : C, 69.36; H, 6.54; N, 17.03. Found: C, 67.72; H, 6.50; N, 16.80.

Biacetyldihydrazone, BdH.—The following method is an improvement over that followed by Busch and Bailar (7). Biacetyl (43.0 g, 0.050 mole) was added slowly with constant stirring to an excess of anhydrous hydrazine (65 g, 2.0 moles). The mixture was cooled in an ice bath, and the product was collected on a sintered glass filter, washed with cold absolute ethanol followed by ether, and dried over  $P_4O_{10}$  in vacuo. Yield, 78 per cent.

Tris(biacetyldihydrazone)cobalt(II) bromide,  
 $[Co(BdH)_3]Br_2$ .—A solution of anhydrous cobalt(II) bromide (2.19 g, 0.0100 mole) in warm absolute ethanol (20 ml) was added slowly with constant stirring to a warm solution of excess biacetyldihydrazone (5 g, 0.05 mole) in 75 ml of ethanol and 75 ml of methanol. The dark brown product which slowly formed was collected on a sintered glass filter, washed with absolute ethanol followed by ether, and dried over  $P_4O_{10}$  in vacuo. Anal. calcd. for  $CoC_{12}H_{30}N_{12}Br_2$ : C, 25.68; H, 5.39; N, 29.95. Found: C, 25.89; H, 5.46; N, 29.73.

Tris(biacetyldihydrazone)cobalt(II) iodide,  
 $[Co(BdH)_3]I_2$ .—This product was prepared by the method of



Stoufer and Busch (53). Anal. calcd. for  $\text{CoC}_{12}\text{H}_{30}\text{N}_{12}\text{I}_2$ : C, 22.00; H, 4.62; N, 25.65. Found: C, 22.19; H, 4.52; N, 25.37.

Tris(biacetyldihydrazone)cobalt(II) nitrate,  $[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$  using biacetyldihydrazone. Yield, 65 per cent. Anal. calcd. for  $\text{CoC}_{12}\text{H}_{30}\text{N}_{14}\text{O}_6$ : C, 27.43; H, 5.76; N, 37.32. Found: C, 27.57; H, 5.56; N, 37.30.

Tris(biacetyldihydrazone)cobalt(II) perchlorate,  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$  using cobalt(II) perchlorate hexahydrate. The green product was washed thoroughly with warm absolute ethanol followed by ether. Yield, 90 per cent. Anal. calcd. for  $\text{CoC}_{12}\text{H}_{30}\text{N}_{12}\text{Cl}_2\text{O}_8$ : C, 24.01; H, 5.04; N, 28.00. Found: C, 24.25; H, 5.16; N, 27.73.

Tris(biacetyldihydrazone)cobalt(II) tetraphenylboron,  $[\text{Co}(\text{BdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  using biacetyldihydrazone. Yield, 90 per cent. Anal. calcd. for  $\text{CoC}_{60}\text{H}_{70}\text{N}_{12}\text{B}$ : C, 70.03; H, 6.86; N, 16.33. Found: C, 68.53; H, 6.61; N, 16.11.

Bis(terpyridine)cobalt(II) chloride pentahydrate,

$[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .—This product was prepared by the method of Hogg and Wilkins (34). Anal. calcd. for  $\text{CoC}_{30}\text{H}_{22}\text{N}_6\text{Cl}_2\text{O}_5$ : C, 52.49; H, 4.70; N, 12.24. Found: C, 52.27; H, 4.80; N, 12.07.

Bis(terpyridine)cobalt(II) chloride tetrahydrate,

$[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  using anhydrous cobalt(II) chloride and terpyridine. Yield, 65 per cent. Anal. calcd. for  $\text{CoC}_{30}\text{H}_{30}\text{N}_6\text{Cl}_2\text{O}_4$ : C, 53.90; H, 4.52; N, 12.57. Found: C, 54.07; H, 4.34; N, 12.28.

Bis(terpyridine)cobalt(II) bromide monohydrate,

$[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ .—This product was prepared by the method of Morgan and Burstall (39). Anal. calcd. for  $\text{CoC}_{30}\text{H}_{24}\text{N}_6\text{Br}_2\text{O}$ : C, 51.23; H, 3.44; N, 11.95. Found: C, 50.95; H, 3.59; N, 11.67.

Bis(terpyridine)cobalt(II) iodide monohydrate,

$[\text{Co}(\text{terpy})_2]\text{I}_2 \cdot \text{H}_2\text{O}$ .—This product was prepared by the method of Morgan and Burstall (39). Anal. calcd. for  $\text{CoC}_{30}\text{H}_{24}\text{N}_6\text{I}_2\text{O}$ : C, 45.31; H, 2.79; N, 10.57. Found: C, 45.02; H, 2.91; N, 10.32.

Bis(terpyridine)cobalt(II) nitrate,

$[\text{Co}(\text{terpy})_2](\text{NO}_3)_2$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$  using

terpyridine. The yield of the brown product was about 60 per cent. Anal. calcd. for  $\text{CoC}_{30}\text{H}_{22}\text{N}_8\text{O}_6$ : C, 55.48; H, 3.41; N, 17.25. Found: C, 54.97, 54.98; H, 3.46, 3.65; N, 16.93, 17.11.

Bis(terpyridine)cobalt(II) perchlorate,

$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$ .—This product was prepared by a method analogous to that used for  $[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$  using terpyridine. The light orange-brown product was collected on a sintered glass filter, washed with absolute ethanol followed by ether, and dried over  $\text{P}_4\text{O}_{10}$  in vacuo. Yield, 80 per cent. Anal. calcd. for  $\text{CoC}_{30}\text{H}_{22}\text{N}_6\text{Cl}_2\text{O}_8$ : C, 49.74; H, 3.06; N, 11.60. Found: C, 49.90; H, 3.20; N, 11.40.

Bis(terpyridine)cobalt(II) perchlorate monohydrate,

$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ .—A solution of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.83 g, 0.0050 mole) in water (30 ml) was added slowly with constant stirring to a warm solution of terpyridine (2.33 g, 0.010 mole) in equal parts of water, ethanol, and methanol (30 ml total). The orange-brown product which formed immediately was collected on a sintered glass filter, washed with water, absolute ethanol, and ether, in that order. It was dried over  $\text{P}_4\text{O}_{10}$  in vacuo. Yield, 90 per cent. Anal. calcd. for  $\text{CoC}_{30}\text{H}_{24}\text{N}_6\text{Cl}_2\text{O}_9$ : C, 48.53; H, 3.26; N, 11.32. Found: C, 48.38; H, 3.14; N, 11.08.

Anoxic bis(terpyridine)cobalt(II) perchlorate monohydrate,  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ .—This product was prepared by decreasing the atmospheric pressure over bis(terpyridine)-cobalt(II) perchlorate monohydrate. The anoxic compound is darker in color than the compound exposed to air. Anal. calcd. for  $\text{CoC}_{30}\text{H}_{24}\text{N}_6\text{Cl}_2\text{O}_9$ : C, 48.53; H, 3.26; N, 11.32. Found: C, 48.67; H, 3.55; N, 11.13. (Analysis of this compound was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.)

Bis(terpyridine)cobalt(II) tetraphenylboron,  $[\text{Co}(\text{terpy})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ .—To an aqueous solution of  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  (1.3 g, 0.0019 mole) was added an aqueous solution of sodium tetraphenylboron (1.2 g, 0.0038 mole). The mixture thickened immediately, and the addition of a small amount of ethanol caused the formation of a light orange very finely divided precipitate. The product was collected on a sintered glass filter, dried overnight, and then washed with absolute ethanol followed by ether. The material was then dried over  $\text{P}_4\text{O}_{10}$  in vacuo. Yield, about 60 per cent. Anal. calcd. for  $\text{CoC}_{78}\text{H}_{69}\text{N}_6\text{B}$ : C, 81.24; H, 5.42; N, 7.29. Found: C, 79.17; H, 5.23; N, 7.38.

Bis(terpyridine)cobalt(II) sulfate dihydrate,  $[\text{Co}(\text{terpy})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .—A solution of cobalt(II) sulfate heptahydrate (1.41 g, 0.0050 mole) in warm water was added slowly with constant stirring to a mixture of hot water and

terpyridine (2.33 g, 0.010 mole). The mixture was heated above the melting point of terpyridine (88°C) for several minutes while stirring continued. The mixture was allowed to cool and a small amount of unreacted terpyridine was filtered off. The slow addition of acetone caused the formation of very shiny red-brown crystals. The product was collected on a sintered glass filter, and washed thoroughly with hot absolute ethanol. The product was recrystallized several times by dissolving in methanol and then adding acetone dropwise. The material was dried over  $P_4O_{10}$  in vacuo. Anal. calcd. for  $CoC_{30}H_{26}N_6SO_6$ : C, 54.80; H, 3.99; N, 12.78. Found: C, 55.38; H, 4.60; N, 12.48.

All analytical measurements were made by Galbraith Microanalytical Laboratories, Knoxville, Tennessee, unless otherwise noted. The analyses of the three complexes containing the tetraphenylboron anion and the one complex containing the sulfate anion were not as close to the calculated values as desired. Nevertheless, these compounds are included because of the importance of the size of the tetraphenylboron anion and the charge of the sulfate anion.

The complexes containing terpyridine appear to be stable in air. All of the complexes containing pyruvaldihydrazone or biacetyldihydrazone decompose in air, some considerably more rapidly than others. Those with the largest anions were the most stable.



## Apparatus

### Magnet

The magnetic susceptibilities were determined by the Gouy method. The equipment has been described previously (13). The magnet used was a Varian Associates Model V-40004 equipped with four-inch cylindrical pole pieces, separated by an air gap of 2-1/4 inches. A Varian Associates Model V-2301-A current regulator was used to provide a constant current ( $\pm 1 \times 10^{-3}$  amp). The maximum field strength attained was  $6812 \pm 40$  oersteds. The magnetic field was calibrated by using water, solid nickel ammonium sulfate hexahydrate, tris(ethylenediamine)nickel(II) thiosulfate (16), and mercury(II) tetrathiocyanatocobaltate(II) (38).

### Cryostat and temperature control

The cryostat and temperature control apparatus used were of the basic design of Figgis and Nyholm (24,25). Temperatures between 100° and 400° K could be controlled with less than 0.1 degree fluctuation.

### Sample tubes

Separate sample tubes were used for solution and solid state measurements. For magnetic measurements of the solids, a quartz tube, approximately 3.5 mm inside diameter and approximately 19.0 cm in length, was suspended in the cryostat from a semi-micro balance by a diamagnetic gold

chain attached to a tapered Teflon plug. The diamagnetic correction of the tube was measured as a function of the temperature between 100° and 400° K. For solution magnetic measurements, a pyrex tube, approximately 15.6 mm inside diameter and approximately 21.0 cm in length, was suspended from the balance into a large glass tube which protected the sample tube from air currents. Measurements were made on solutions of known concentration. The diamagnetic correction for the sample tube filled with pure solvent was subtracted from the observed change in apparent weight.

#### Balance

A Mettler Model B-6 semi-micro balance of 0.01 mg sensitivity was used to measure the force exerted by the magnetic field upon the sample.

#### Spectrometers

The solid state electronic spectral measurements were obtained by using a Cary Model 14 recording spectrophotometer with a Cary Model 1411 Diffuse Reflectance Accessory. Magnesium carbonate was used as the reference. Infrared spectra were obtained using a Beckman Model IR-10 equipped with sodium chloride optics and calibrated with polystyrene. Both the Nujol mull and pressed potassium bromide pellet technique were used.



### Conductance apparatus

All conductances were measured using an Industrial Instruments, Inc., Model RC-18 Conductivity Bridge and a cell with a constant of  $1.485 \text{ cm}^{-1}$ . A constant temperature of  $25.0^\circ\text{C} \pm 0.01^\circ$  was maintained by the use of a silicone oil bath, regulated by a Sargent Thermonitor, Model SW. Concentrations of approximately  $2 \times 10^{-2} \text{ M}$  in reagent grade dimethyl sulfoxide were used. This dimethyl sulfoxide had a conductance of less than  $8 \times 10^{-7} \text{ mhos cm}^{-1}$ .

### X-ray diffraction apparatus

The X-ray diffraction patterns were obtained by the use of a Phillips Electronic Instruments Recording Diffractometer equipped with a copper target. A curved single crystal monochromator was used to reduce fluorescence. Low temperatures of approximately  $-50^\circ\text{C} \pm 5^\circ$  were obtained by passing a stream of gaseous nitrogen through a copper coil submerged in liquid nitrogen and then onto the sample. Temperatures of approximately  $+45^\circ\text{C} \pm 3^\circ$  were obtained by passing gaseous nitrogen through a heated copper tube and then onto the sample.

### Electron paramagnetic resonance spectrometer

The equipment used has been described previously (50). A Varian Associates electron paramagnetic resonance spectrometer system, V-4502-14, was used. The system consists of a V-4501 console, a V-4500-41A microwave bridge, a V-4500

100 Kc field modulation and control unit, a V-3601 twelve-inch magnet, and a V-Fr2503 magnet power supply unit. A V-4531 multi-purpose cavity was used in combination with a variable temperature accessory V-4557.

## RESULTS

### Magnetic Measurements

The room-temperature magnetic moments of the solids and their solutions prepared during the course of this investigation are listed in Table 2. All magnetic measurements were obtained at two different field strengths, namely, 6812 and 5724 oersteds. The close agreement of the magnetic moments at different field strengths indicates that metal-metal interaction does not exist in any of the complexes (38). For solution magnetic measurements, concentrations of 0.020 molar in dimethyl sulfoxide or water were used. The data given are averages of two or more separate measurements on different portions of the same solution. The solvent was dimethyl sulfoxide unless otherwise noted.

The acetylacetonate complex of iron(III) was chosen as a reference standard for the solution magnetic measurements. It is an uncharged complex and consequently there is no anion which might possibly affect the magnetic behavior. The magnetic moment of solid is reported to be 5.95 B.M. (10). The solution magnetic moment was found in the present investigation to be 5.93 and 5.90 B.M. in two

TABLE 2

MAGNETIC MOMENTS OF SOLIDS AND SOLUTIONS AT ROOM TEMPERATURE

Complex	Solid		Solution	
	$\mu_{\text{eff}}^a$	$\mu_{\text{eff}}^b$	$\mu_{\text{eff}}^a$	$\mu_{\text{eff}}^b$
$[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$	4.10	4.11	4.78	4.80
$[\text{Co}(\text{PvdH})_3]\text{Br}_2$	4.23	4.23	4.73	4.70
$[\text{Co}(\text{PvdH})_3]\text{I}_2$	4.41	4.40	4.84	4.83
$[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$	4.50	4.49	4.74	4.72
$[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$	4.40	4.40	4.81	4.79
$[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$	3.04	3.03	4.62	4.59
$[\text{Co}(\text{BdH})_3]\text{Br}_2$	4.26	4.26	4.57	4.54
$[\text{Co}(\text{BdH})_3]\text{I}_2$	4.07	4.07	4.61	4.54
$[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$	4.34	4.34	4.59	4.57
$[\text{Co}(\text{BdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$	3.61	3.61	4.65	4.65
$[\text{Co}(\text{terpy})_2](\text{NO}_3)_2^c$	2.96	2.96	3.29	3.23
$[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}^c$	2.41	2.41	3.31	3.29
$[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}^c$	2.51	2.52	3.21	3.18
$[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$	2.61	2.61	3.27	3.25
$[\text{Co}(\text{terpy})_2]\text{I}_2 \cdot \text{H}_2\text{O}$	3.30	3.30	3.51	3.49
$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$	4.05	4.04	3.35	3.31
$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	4.21	4.20	3.40	3.35
$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (anoxic)	3.84	3.83	—	—

Table 2 (cont'd)

Complex	Solid		Solution	
	$\mu_{\text{eff}}^{\text{a}}$	$\mu_{\text{eff}}^{\text{b}}$	$\mu_{\text{eff}}^{\text{a}}$	$\mu_{\text{eff}}^{\text{b}}$
$[\text{Co}(\text{terpy})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}^{\text{c}}$	2.98	2.98	3.25	3.23
$[\text{Co}(\text{terpy})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$	3.23	3.25	3.21	3.20

<sup>a</sup>Field strength = 6812 oersteds.

<sup>b</sup>Field strength = 5724 oersteds.

<sup>c</sup>Solution moment in water.

independent measurements, indicating excellent precision of measurement of the solution magnetic moments.

The room-temperature magnetic moment of each complex in the solid state is in the region intermediate between normal high-spin and low-spin octahedral cobalt(II) magnetic moments. In order to determine the possibility of a Boltzmann distribution over high- and low-spin states, the magnetic susceptibility of each complex was determined as a function of temperature. The temperature range was from 110° to 350°K or the temperature at which the sample began to decompose. All susceptibilities were corrected for the diamagnetic contribution of the ligands using Pascal's constants, and of the anions, the metal ion, and the water of hydration using experimentally determined values (52) (see Appendix I).

The reciprocal of the corrected magnetic susceptibility versus the absolute temperature are shown in Figures 1 through 19. Tables 3 through 12 contain susceptibility and magnetic moment data for the complexes. The plots for all  $[\text{Co}(\text{PvdH})_3]^{2+}$  complexes (data for  $[\text{Co}(\text{PvdH})_3]\text{Br}_2$  taken from reference (27)) are represented in Figure 20, for all  $[\text{Co}(\text{BdH})_3]^{2+}$  complexes in Figure 21, and for all  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes in Figures 22 and 23. The broken lines represent plots for ideal high- and low-spin cobalt(II) complexes obeying the Curie-Weiss law with Weiss constants of 0°

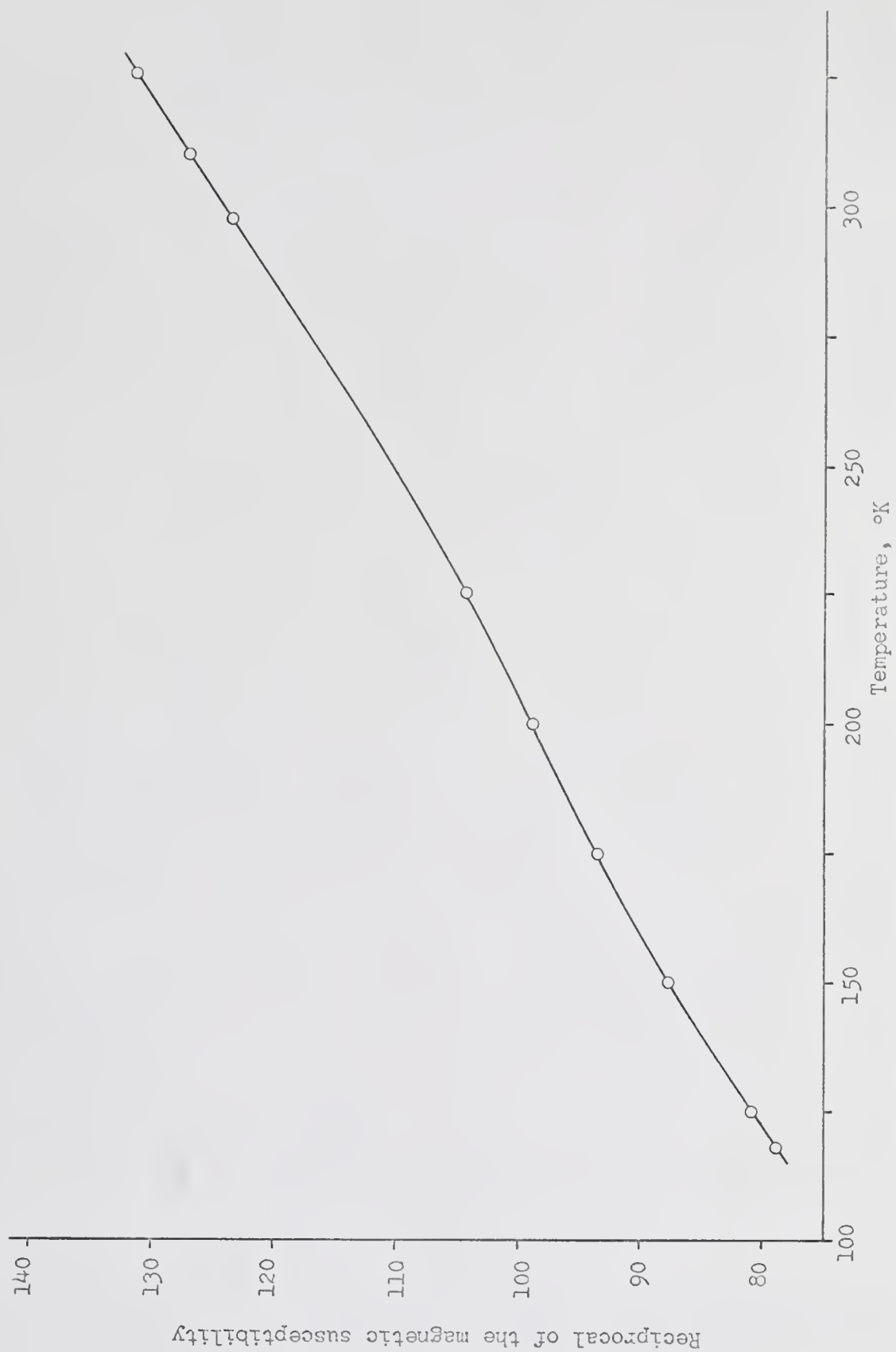


Fig. 1.- Temperature dependent susceptibility of  $[\text{Co}(\text{PvdH})_3]\text{I}_2$



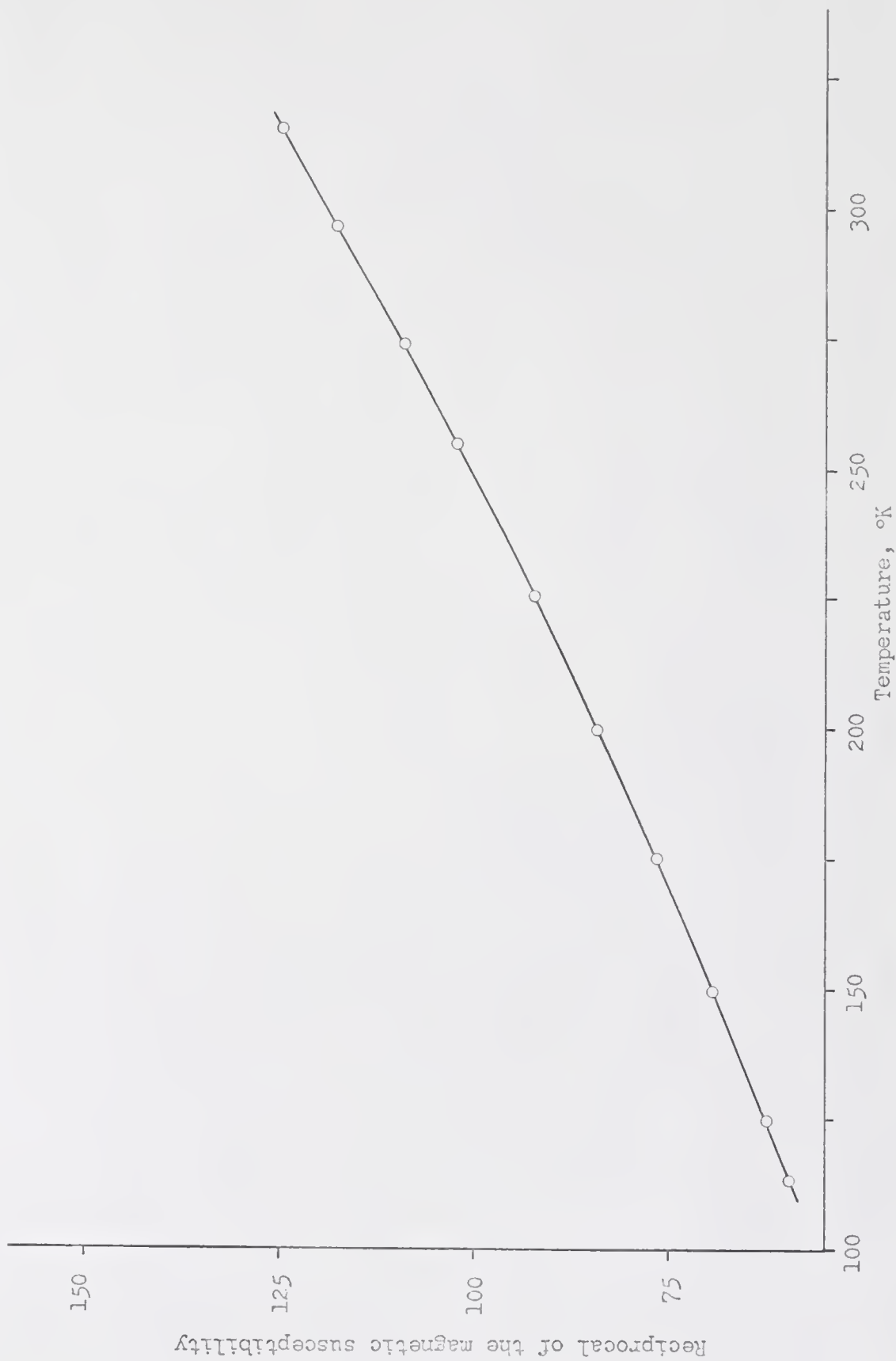


Fig. 2.- Temperature dependent susceptibility of  $[\text{Co}(\text{PvclH})_3](\text{ClO}_4)_2$

TABLE 3

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  AND  $[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$  WITH TEMPERATURE

$[\text{Co}(\text{PvdH})_3]\text{I}_2$			$[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
118.39	12,684	3.48	114.01	16,777	3.93
124.99	12,389	3.53	124.99	16,004	4.02
149.98	11,420	3.72	149.98	14,391	4.17
175.01	10,734	3.89	175.01	13,040	4.29
199.99	10,131	4.04	199.99	11,856	4.37
225.04	9,603	4.17	225.04	10,847	4.44
297.66	8,077	4.40	254.76	9,722	4.47
309.65	7,882	4.44	273.98	9,172	4.50
325.00	7,628	4.47	295.29	8,499	4.50
340.00	7,362	4.49	315.03	8,020	4.51
			334.98	7,578	4.52

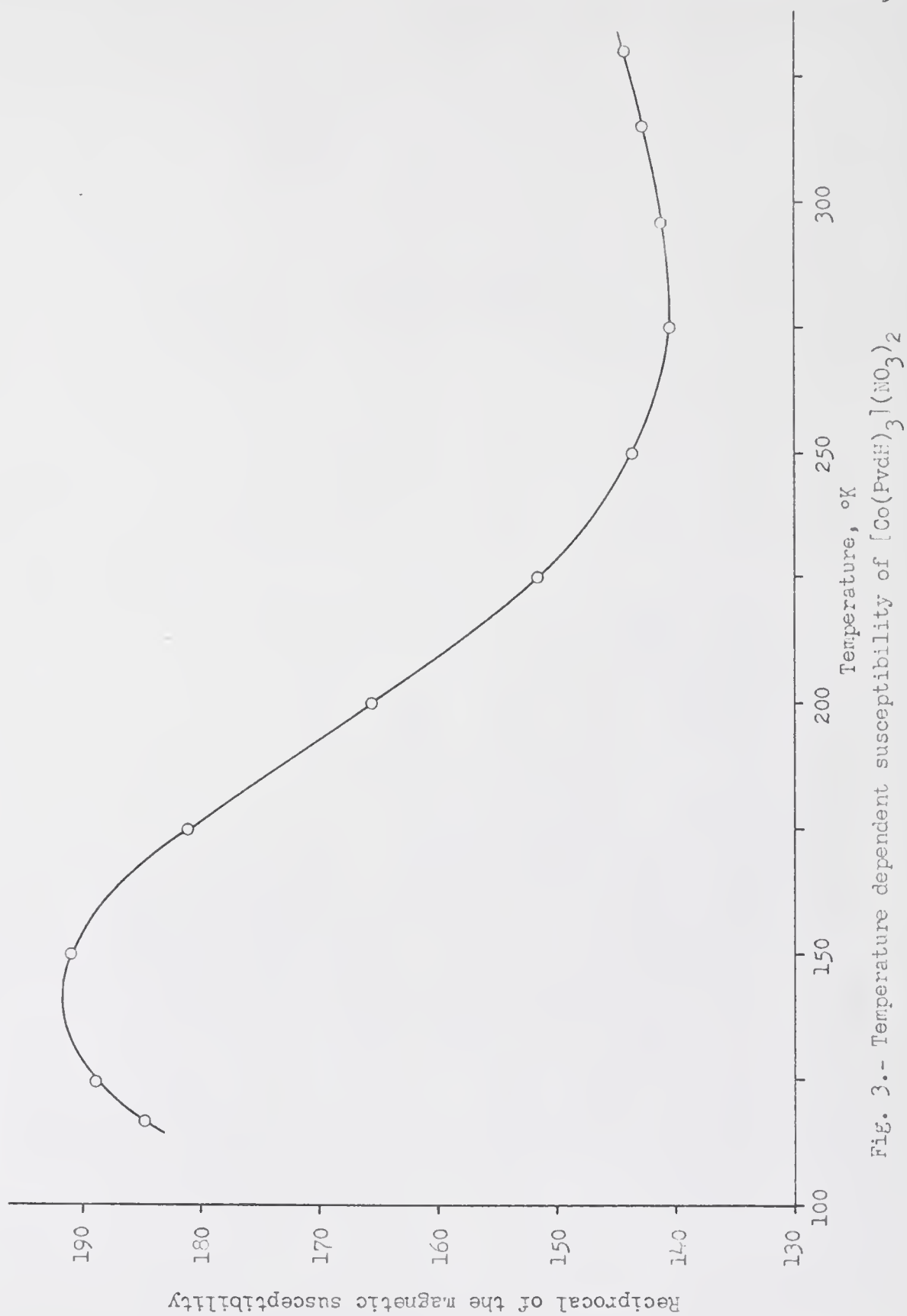


Fig. 3.- Temperature dependent susceptibility of  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$

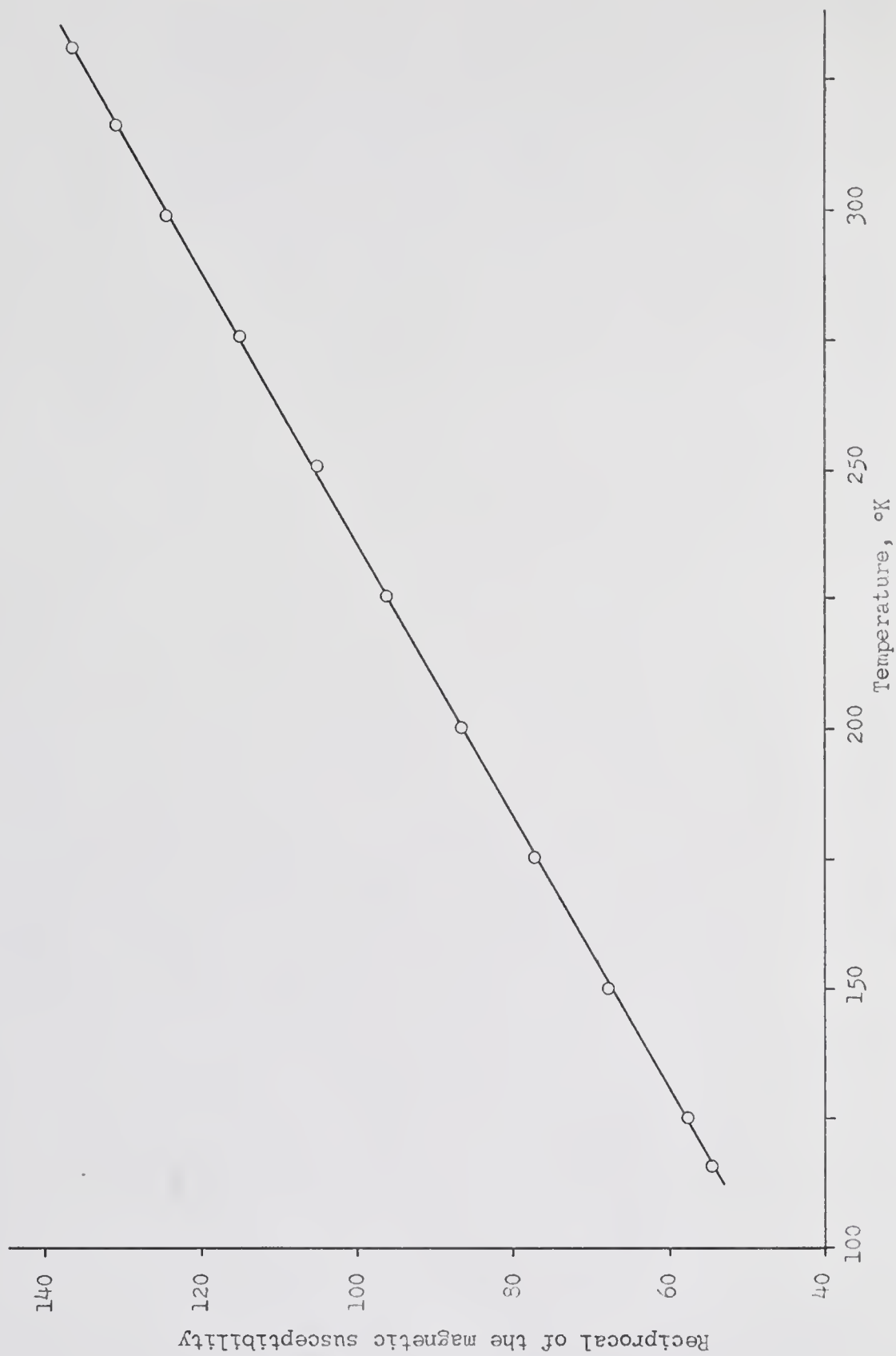


Fig. 4.- Temperature dependent susceptibility of  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$

TABLE 4

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$  AND  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$   
WITH TEMPERATURE

$[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$				$[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$			
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\mu_{\text{eff}}$
116.17	5,412	2.25	116.02	18,367	4.15	116.02	4.15
124.99	5,293	2.31	124.99	17,322	4.18	124.99	4.18
149.98	5,237	2.52	149.98	14,766	4.23	149.98	4.23
175.01	5,520	2.79	175.01	12,939	4.27	175.01	4.27
199.99	6,040	3.12	199.99	11,516	4.31	199.99	4.31
225.04	6,591	3.46	225.04	10,400	4.35	225.04	4.35
250.01	6,957	3.75	250.01	9,487	4.37	250.01	4.37
274.98	7,112	3.97	274.98	8,634	4.38	274.98	4.38
296.08	7,054	4.10	297.95	8,037	4.40	297.95	4.40
315.03	6,999	4.22	315.03	7,633	4.40	315.03	4.40
330.03	6,931	4.29	330.03	7,308	4.41	330.03	4.41
			345.03	7,018	4.42	345.03	4.42

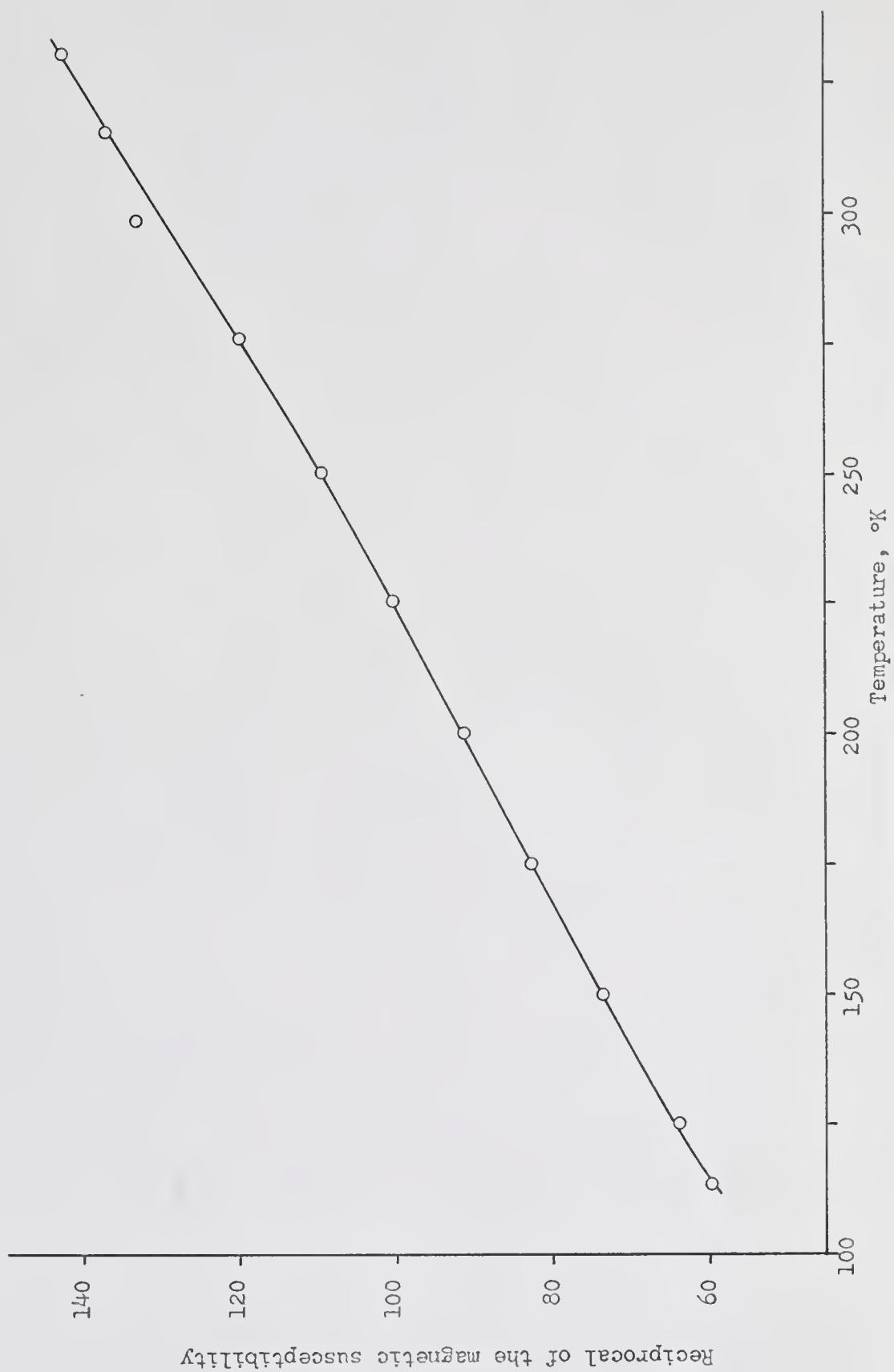


Fig. 5.- Temperature dependent susceptibility of  $[\text{Co}(\text{BdH})_3]\text{Br}_2$



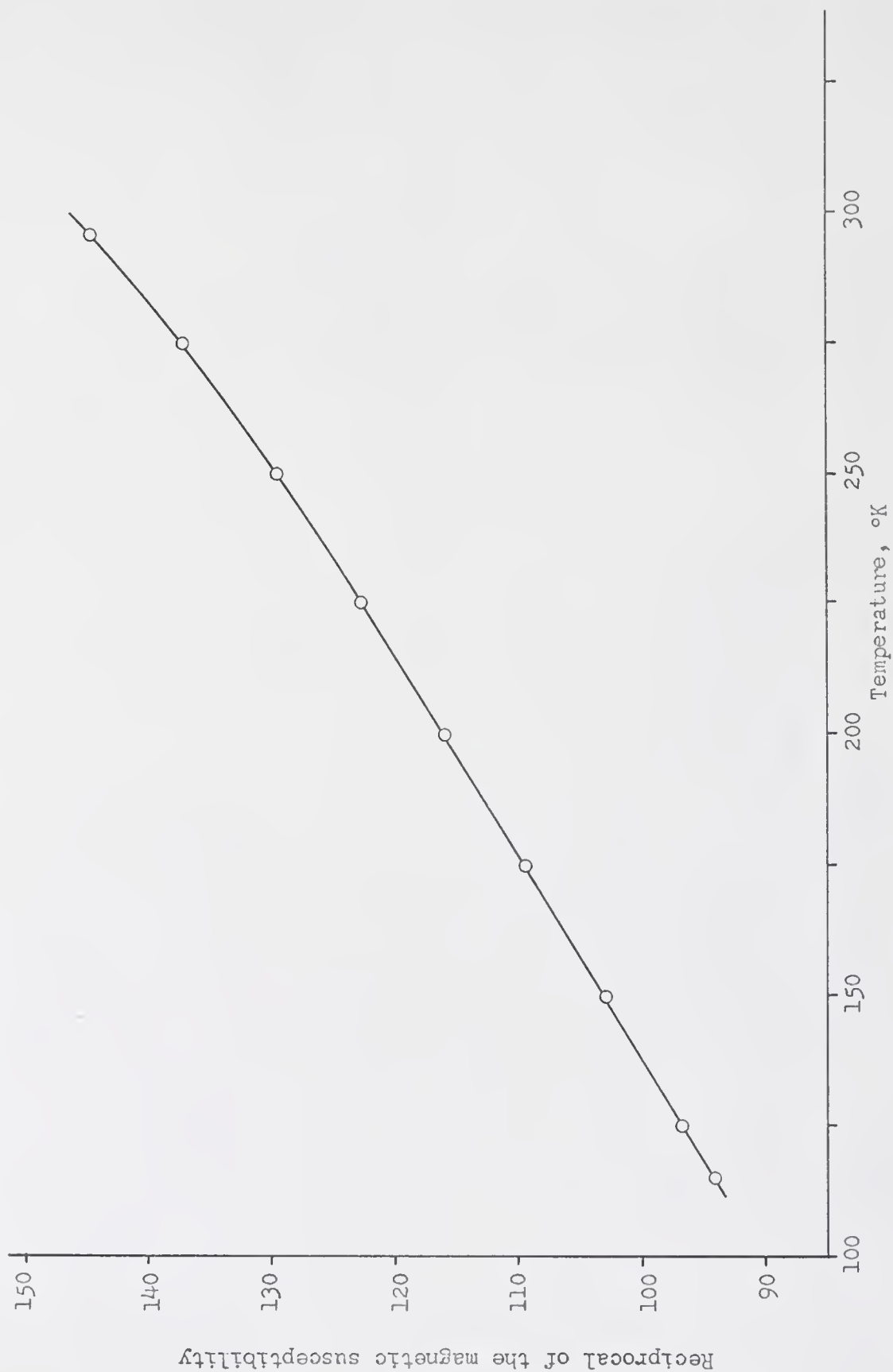


Fig. 6.- Temperature dependent susceptibility of  $[\text{Co}(\text{BdH})_3]\text{I}_2$

TABLE 5

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co}(\text{BdH})_3]\text{Br}_2$  AND  $[\text{Co}(\text{BdH})_3]\text{I}_2$  WITH TEMPERATURE

$[\text{Co}(\text{BdH})_3]\text{Br}_2$			$[\text{Co}(\text{BdH})_3]\text{I}_2$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
114.23	16,789	3.93	115.02	10,657	3.14
124.99	15,684	3.98	124.99	10,355	3.23
149.97	13,665	4.07	149.98	9,724	3.43
175.01	12,146	4.14	175.01	9,159	3.60
199.99	10,989	4.21	199.99	8,648	3.74
225.04	10,010	4.26	225.04	8,171	3.85
250.01	9,192	4.31	250.01	7,733	3.95
276.13	8,390	4.32	275.56	7,316	4.03
315.03	7,326	4.31	296.37	6,951	4.08
330.03	7,044	4.33			
345.03	6,834	4.36			

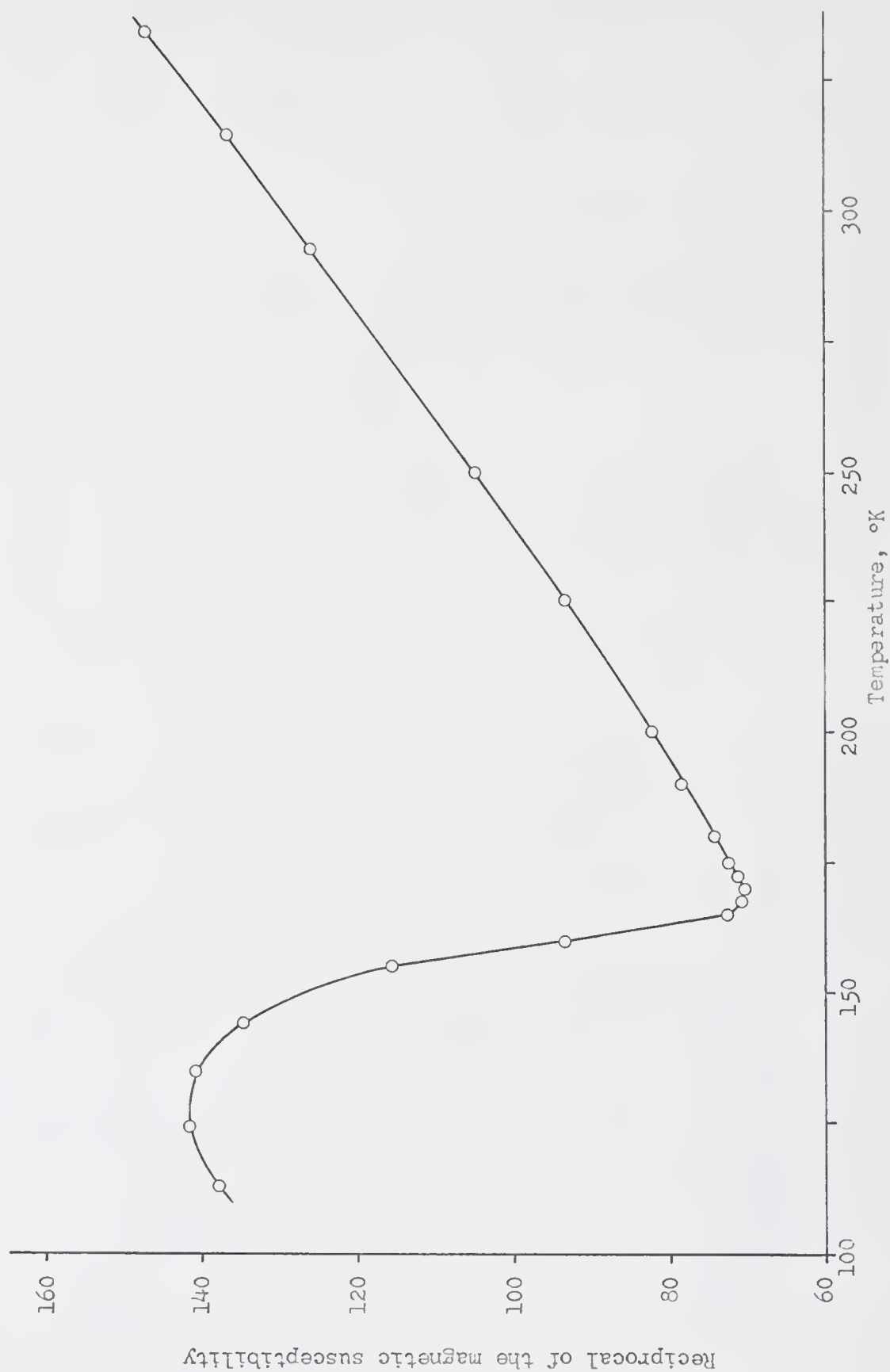


Fig. 7.- Temperature dependent susceptibility of  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$

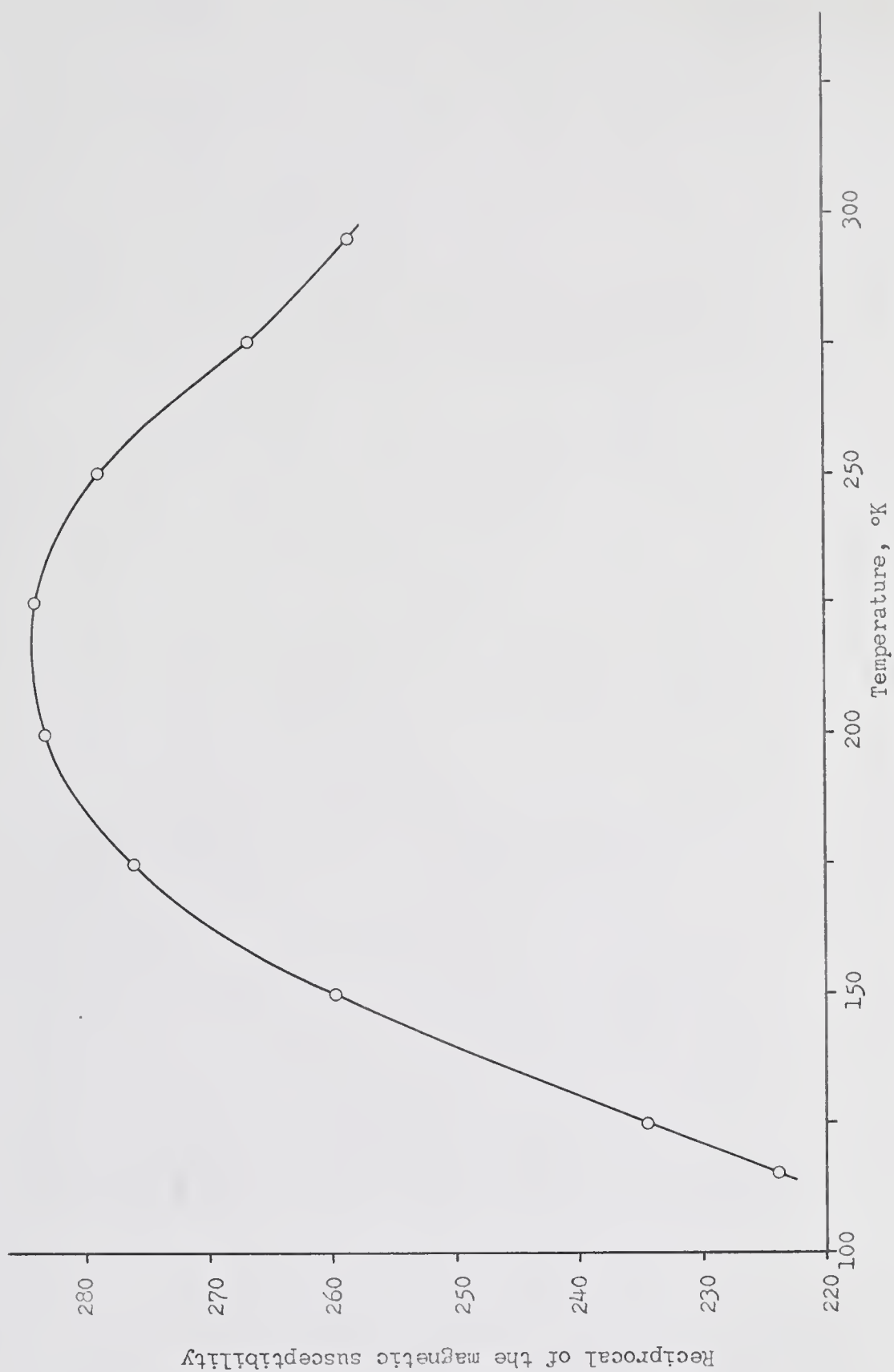


Fig. 8.- Temperature dependent susceptibility of  $[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$

TABLE 6

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$  AND  $[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$   
WITH TEMPERATURE

$[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$			$[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
114.09	7,256	2.58	115.67	4,466	2.04
124.99	7,066	2.67	124.99	4,267	2.07
134.97	7,100	2.78	149.98	3,850	2.16
154.99	8,657	3.29	175.01	3,625	2.26
160.02	10,707	3.72	199.99	3,534	2.39
164.97	13,740	4.28	225.04	3,524	2.53
167.48	14,186	4.38	250.01	3,622	2.70
169.99	14,200	4.41	274.98	3,751	2.89
172.50	14,024	4.42	295.29	3,870	3.04
175.01	13,819	4.42			
179.97	13,475	4.42			
190.01	12,753	4.42			
199.99	12,159	4.43			
225.04	10,736	4.41			
250.01	9,562	4.39			
293.71	7,963	4.34			
334.98	6,816	4.29			
349.98	6,620	4.32			

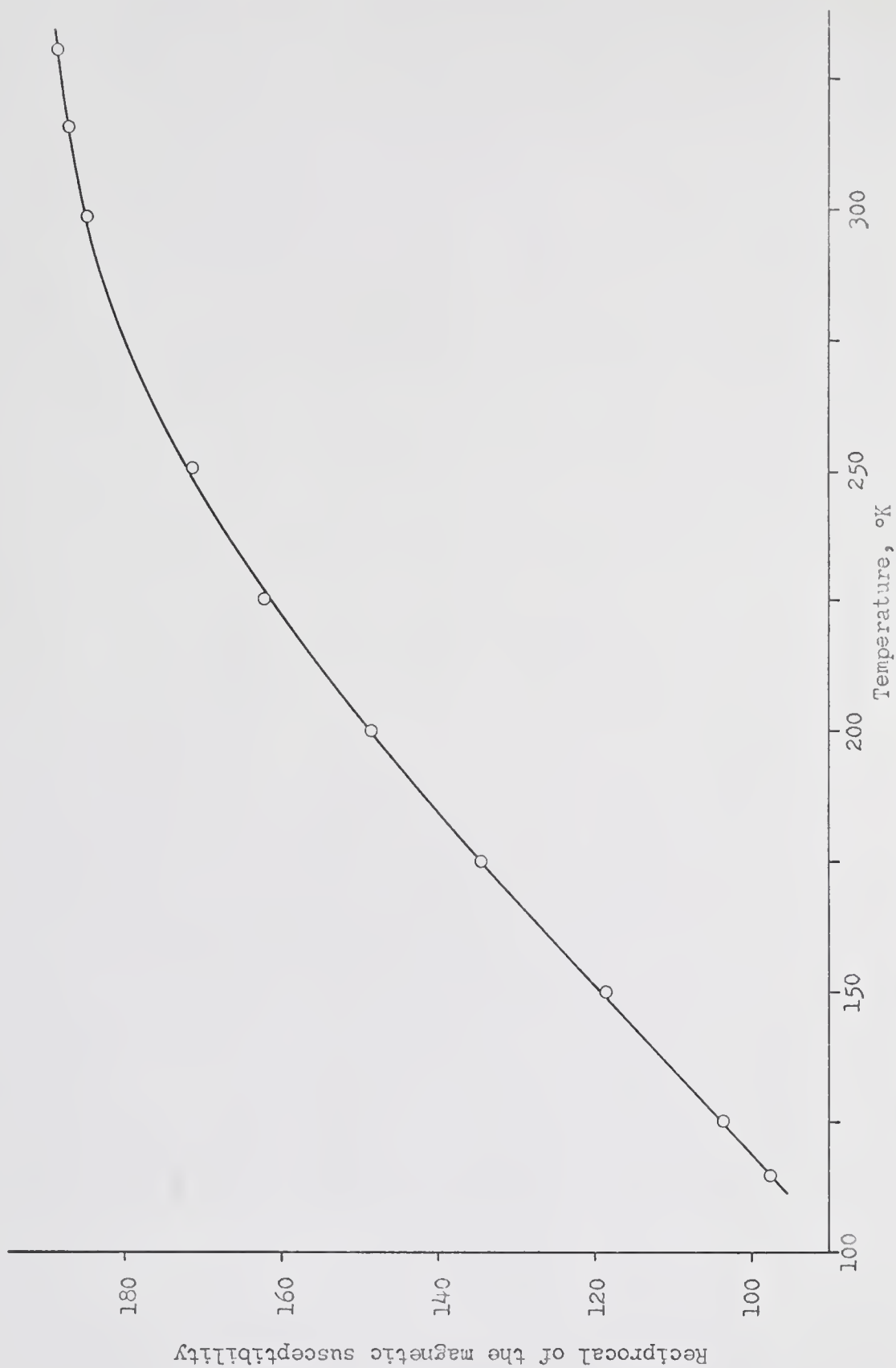


Fig. 9.- Temperature dependent susceptibility of  $[\text{Co}(\text{EdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$



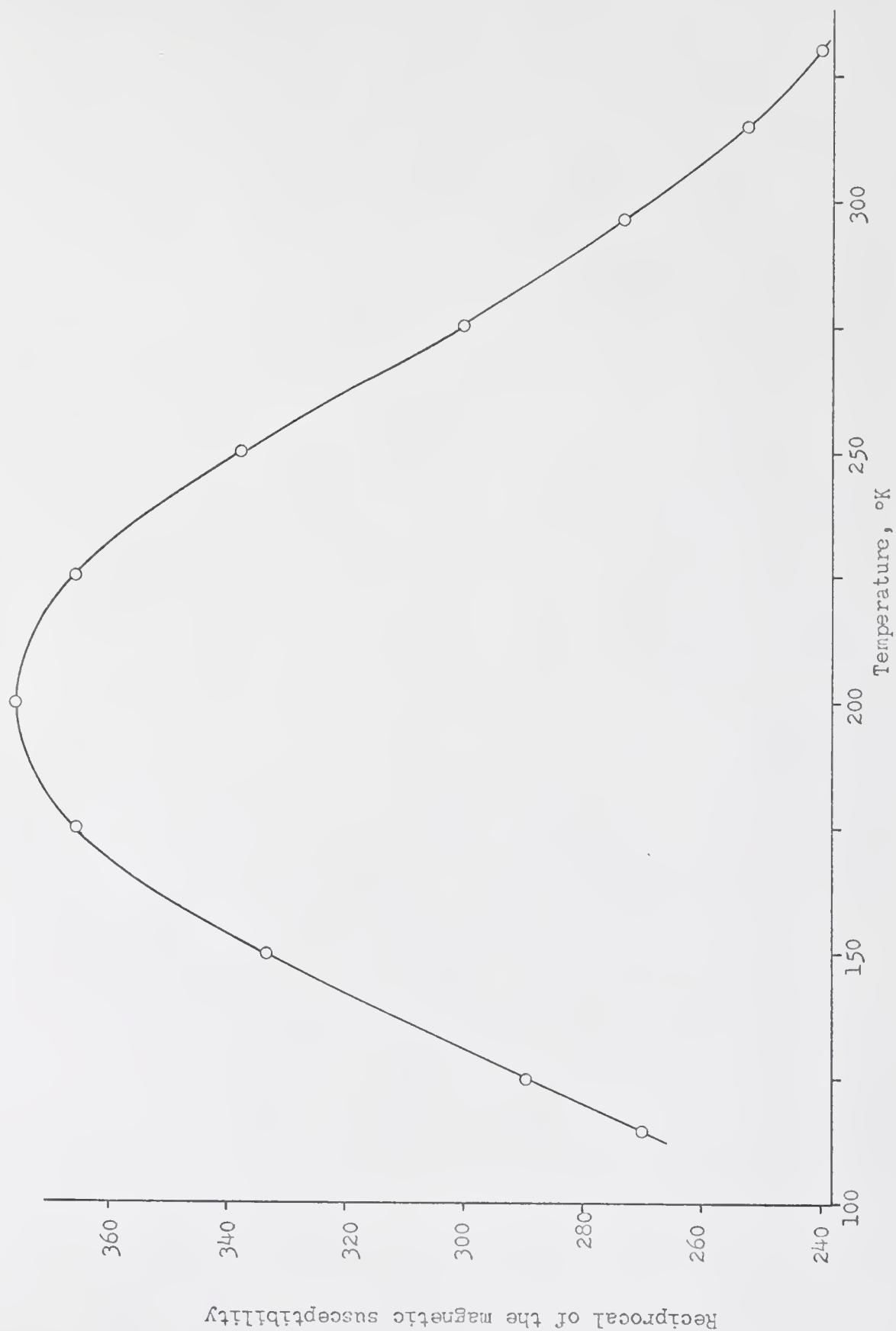


Fig. 10.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2](\text{NO}_3)_2$

TABLE 7

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co}(\text{BdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  AND  $[\text{Co}(\text{terpy})_2](\text{NO}_3)_2$   
WITH TEMPERATURE

$[\text{Co}(\text{BdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$			$[\text{Co}(\text{terpy})_2](\text{NO}_3)_2$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
114.66	10,245	3.08	114.66	3,707	1.85
124.99	9,649	3.12	124.99	3,453	1.87
149.97	8,441	3.20	149.98	2,995	1.90
175.01	7,439	3.24	175.01	2,739	1.97
199.99	6,732	3.29	199.99	2,661	2.07
225.04	6,180	3.35	225.04	2,739	2.23
250.01	5,848	3.43	250.01	2,967	2.45
298.38	5,421	3.61	274.93	3,336	2.72
315.03	5,355	3.69	296.58	3,667	2.96
330.03	5,303	3.76	315.03	3,951	3.17
			330.03	4,169	3.33

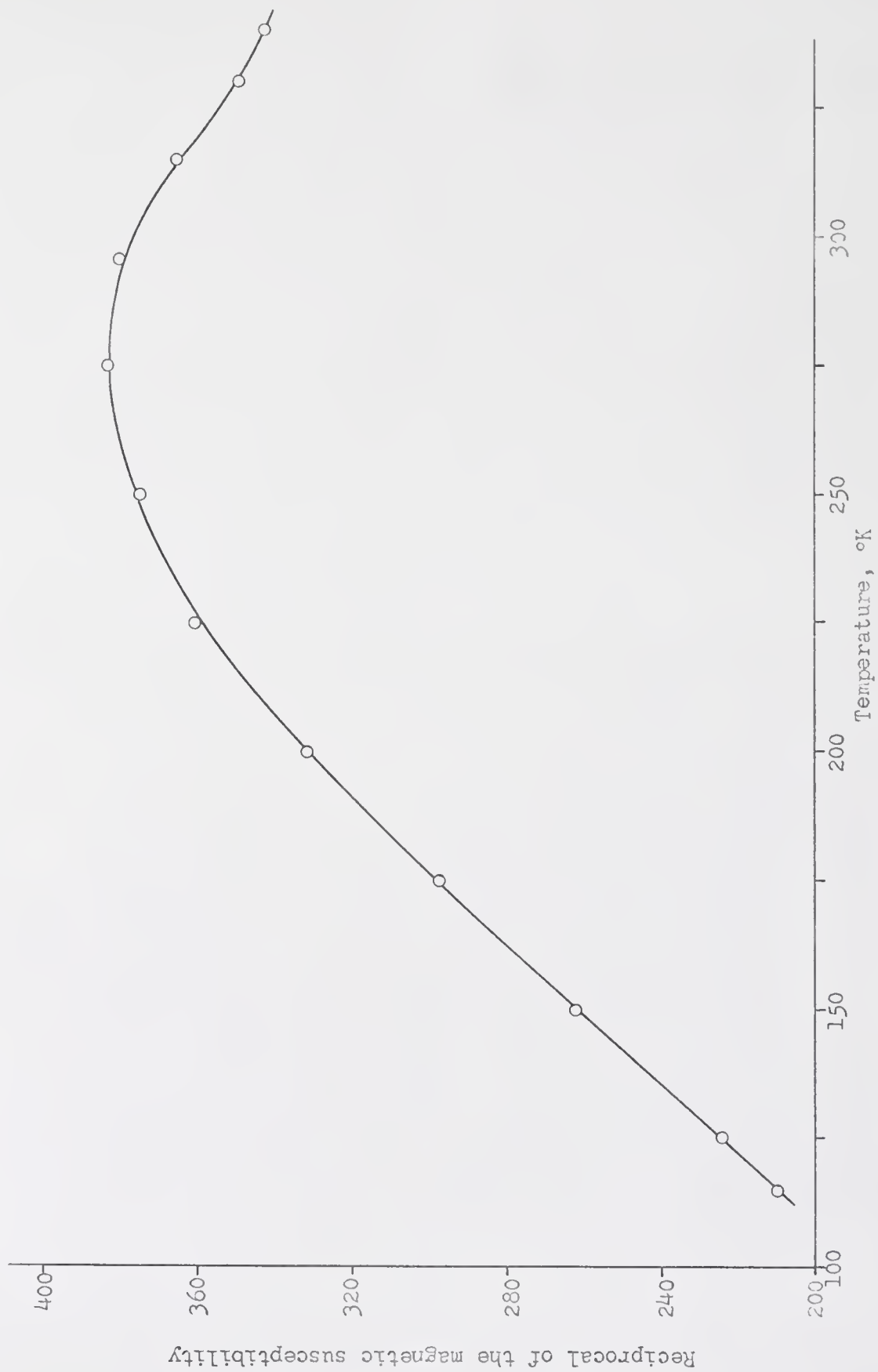


Fig. 11.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$

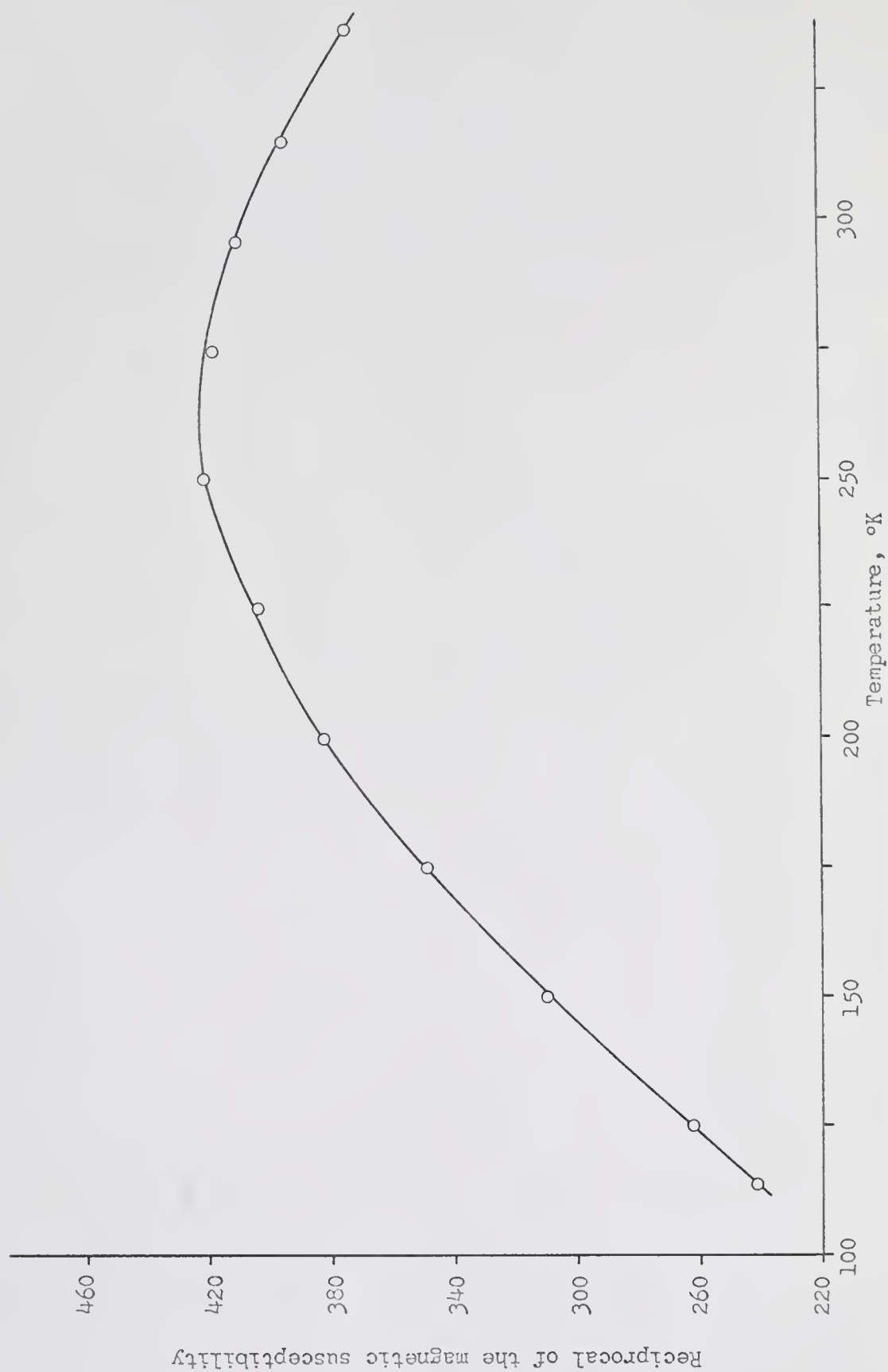


Fig. 12.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

TABLE 8

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co(terpy)}_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  AND  $[\text{Co(terpy)}_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$   
WITH TEMPERATURE

[Co(terpy) <sub>2</sub> ]Cl <sub>2</sub> ·5H <sub>2</sub> O			[Co(terpy) <sub>2</sub> ]Cl <sub>2</sub> ·4H <sub>2</sub> O		
T, °K	χ <sub>c</sub> x 10 <sup>6</sup>	μ <sub>eff</sub>	T, °K	χ <sub>c</sub> x 10 <sup>6</sup>	μ <sub>eff</sub>
115.59	4,722	2.10	113.94	4,133	1.95
124.99	4,454	2.12	124.99	3,810	1.96
149.98	3,814	2.15	149.98	3,228	1.98
175.01	3,363	2.18	175.01	2,870	2.01
199.99	3,018	2.21	199.99	2,617	2.05
225.04	2,776	2.24	225.04	2,478	2.12
250.01	2,668	2.32	250.01	2,378	2.19
274.98	2,609	2.41	274.98	2,393	2.30
296.80	2,633	2.51	296.37	2,438	2.41
315.03	2,739	2.64	315.03	2,532	2.54
330.03	2,864	2.76	334.98	2,671	2.69
340.00	2,923	2.83			
349.98	3,001	2.91			

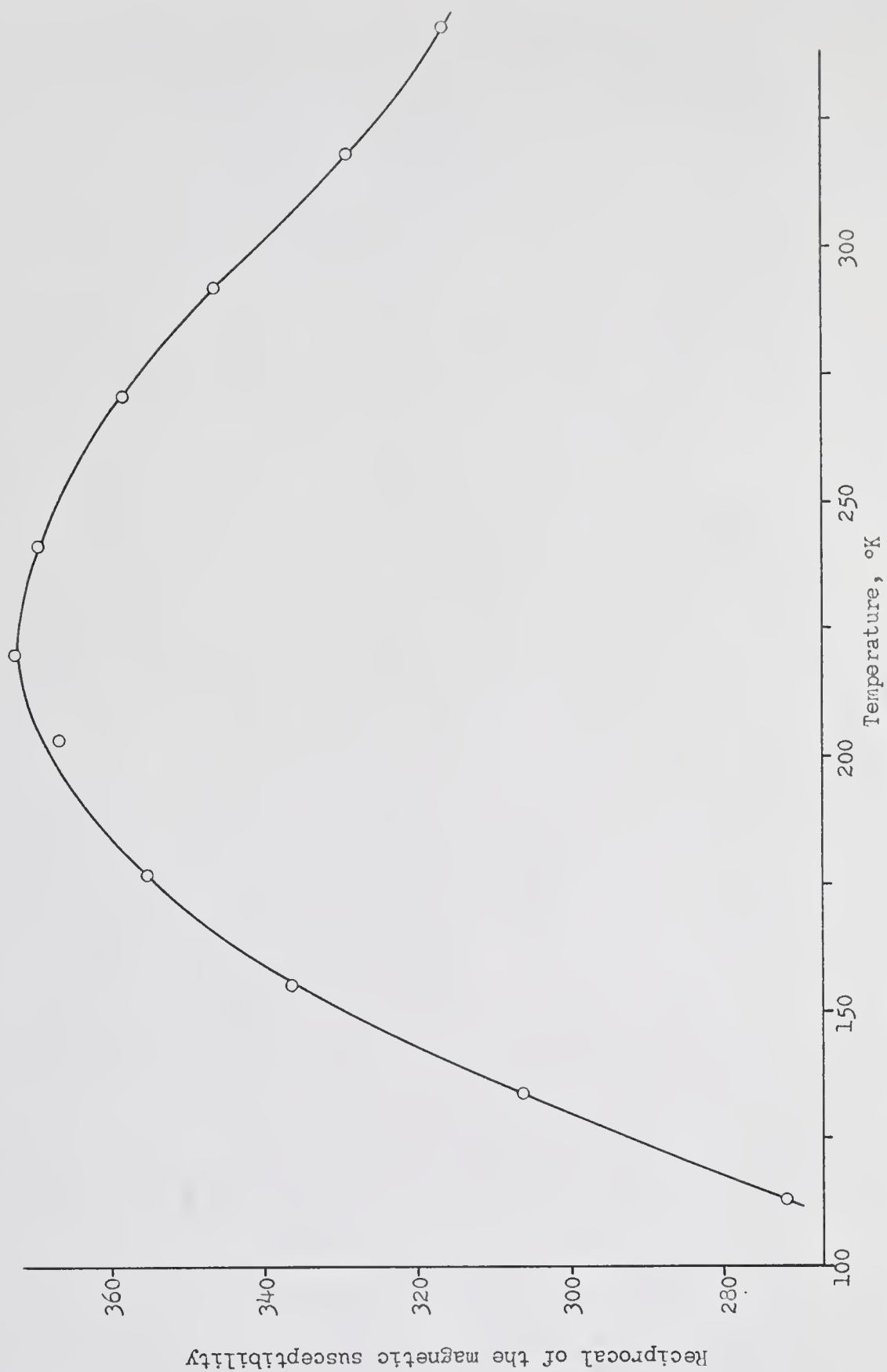


Fig. 13.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$



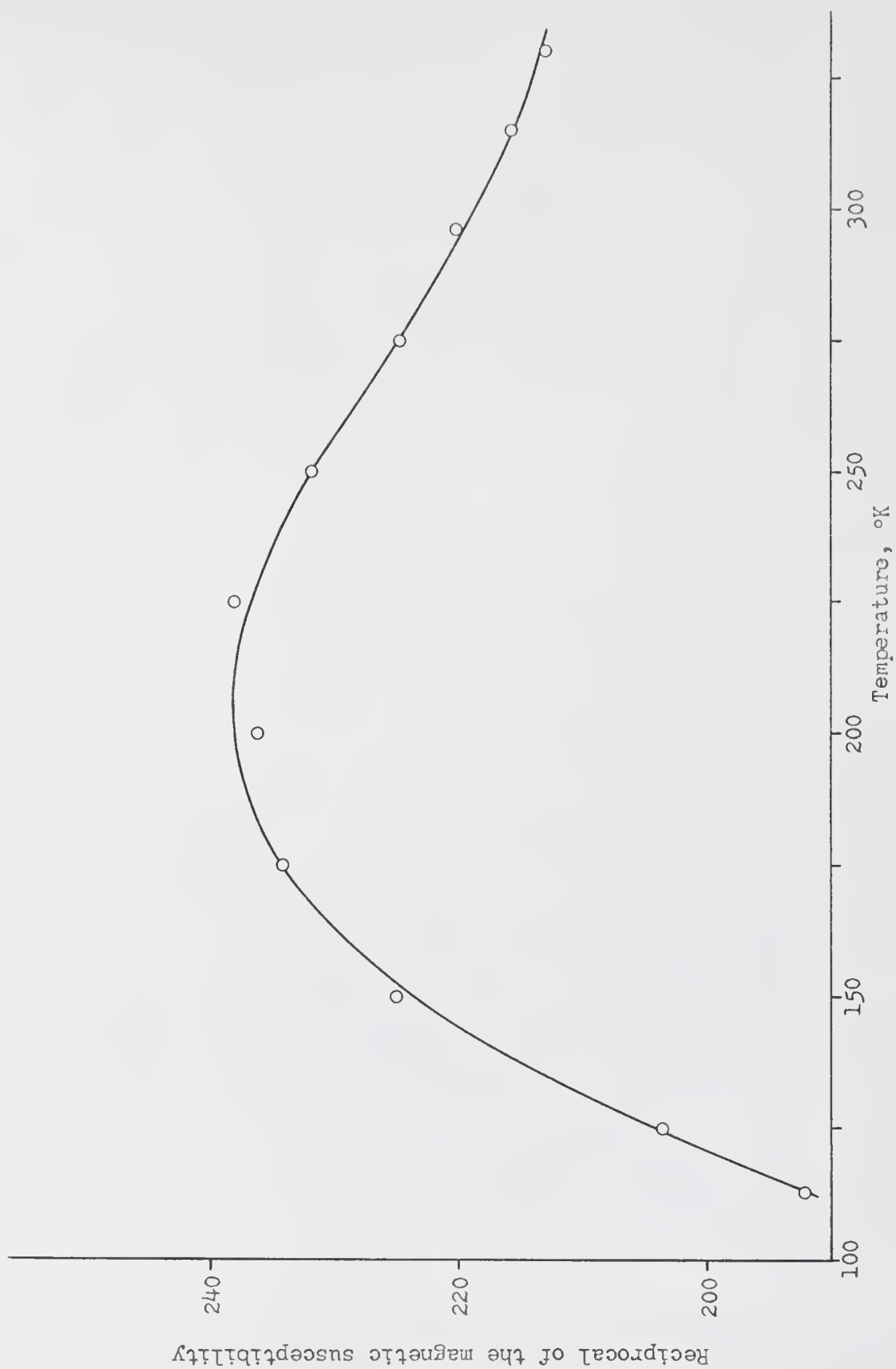


Fig. 14.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2]\text{I}_2 \cdot \text{H}_2\text{O}$

TABLE 9

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co(terpy)}_2]\text{Br}_2\cdot\text{H}_2\text{O}$  AND  $[\text{Co(terpy)}_2]\text{I}_2\cdot\text{H}_2\text{O}$   
WITH TEMPERATURE

$[\text{Co(terpy)}_2]\text{Br}_2\cdot\text{H}_2\text{O}$			$[\text{Co(terpy)}_2]\text{I}_2\cdot\text{H}_2\text{O}$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
112.79	3,678	1.83	113.30	5,205	2.18
134.04	3,260	1.88	124.99	4,912	2.23
155.57	2,974	1.93	149.98	4,448	2.32
177.16	2,815	2.01	175.01	4,266	2.45
198.12	2,727	2.09	199.99	4,238	2.62
220.01	2,688	2.18	225.04	4,205	2.76
241.76	2,710	2.30	250.01	4,315	2.95
270.18	2,793	2.47	274.98	4,454	3.14
291.49	2,890	2.61	296.51	4,542	3.30
317.47	3,040	2.79	315.02	4,636	3.43
342.58	3,158	2.95	330.03	4,697	3.54

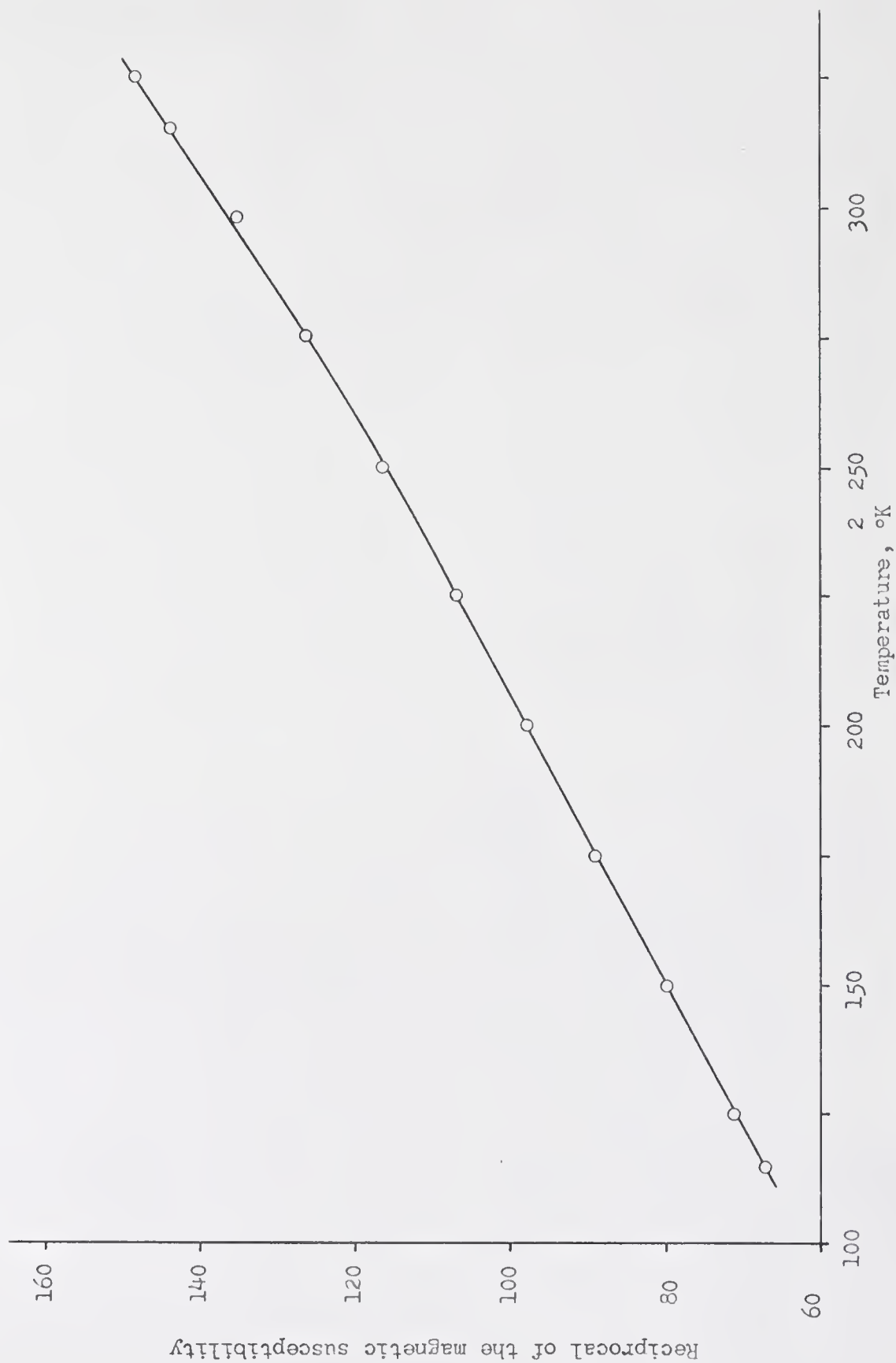


Fig. 15.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

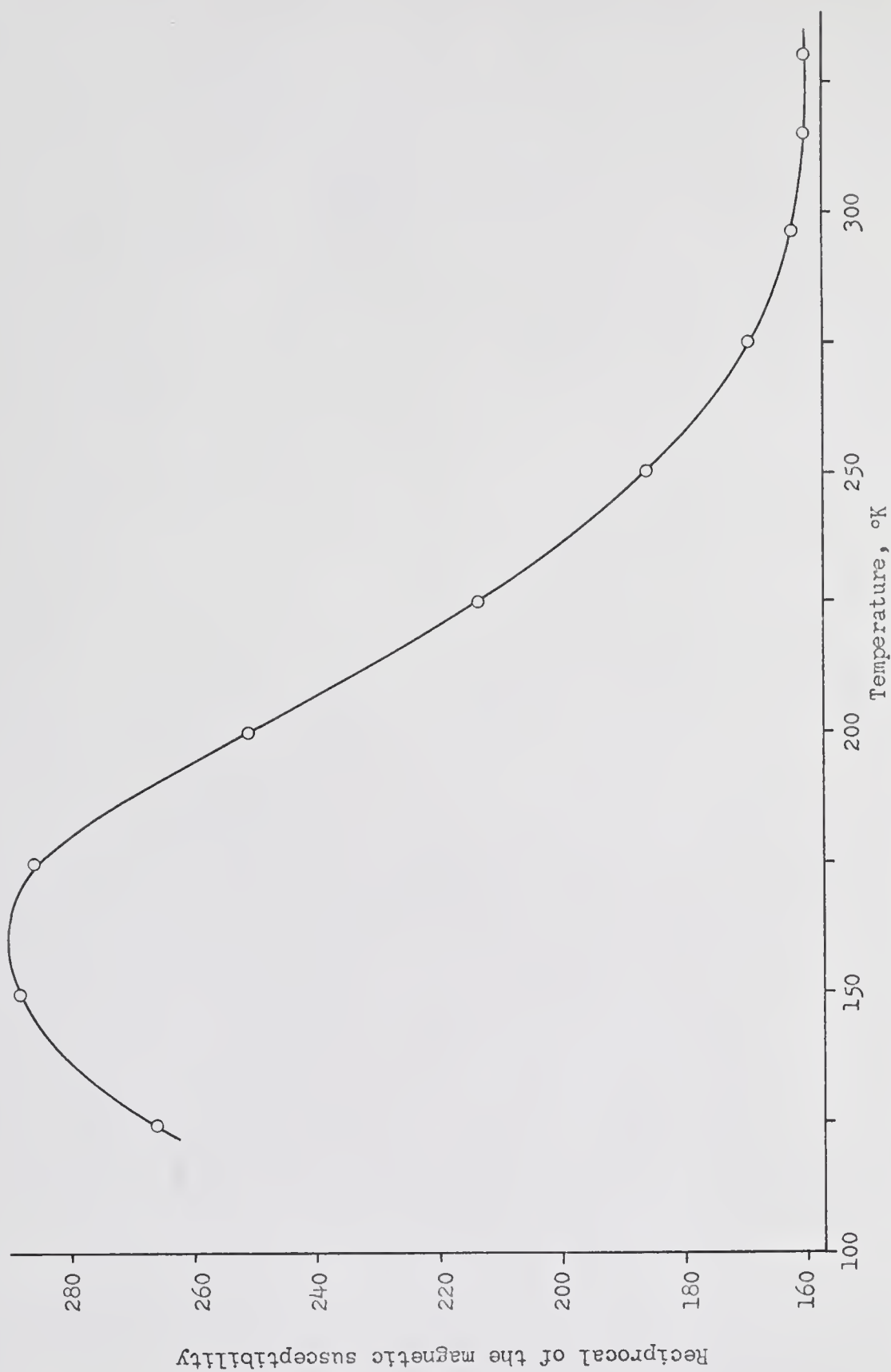


Fig. 16.- Temperature dependent susceptibility of anoxic  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

TABLE 10

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF  
 $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  AND ANOXIC  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$   
 WITH TEMPERATURE

$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$			Anoxic $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$		
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$
115.02	14,895	3.72	127.00	3,759	1.96
124.99	14,116	3.77	149.98	3,479	2.05
149.98	12,552	3.90	175.01	3,501	2.22
175.01	11,276	3.99	199.99	4,000	2.54
199.99	10,256	4.07	225.04	4,692	2.92
225.04	9,370	4.12	250.01	5,384	3.29
250.01	8,618	4.17	274.98	5,911	3.62
274.98	7,940	4.20	296.23	6,169	3.84
296.73	7,411	4.21	315.03	6,268	3.99
315.03	6,989	4.22	330.03	6,268	4.08
325.00	6,771	4.21	299.24	6,230	3.88

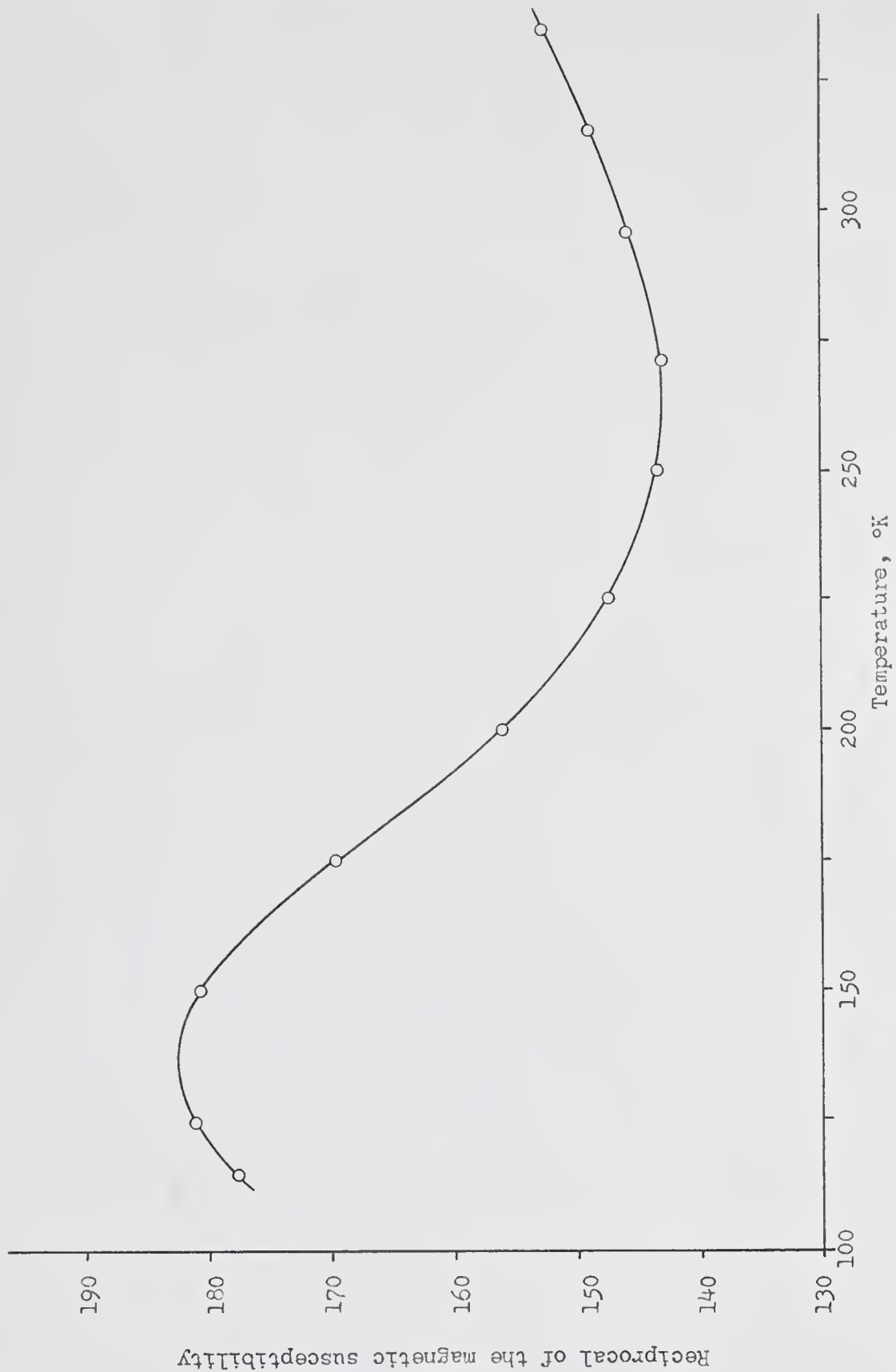


Fig. 17.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$



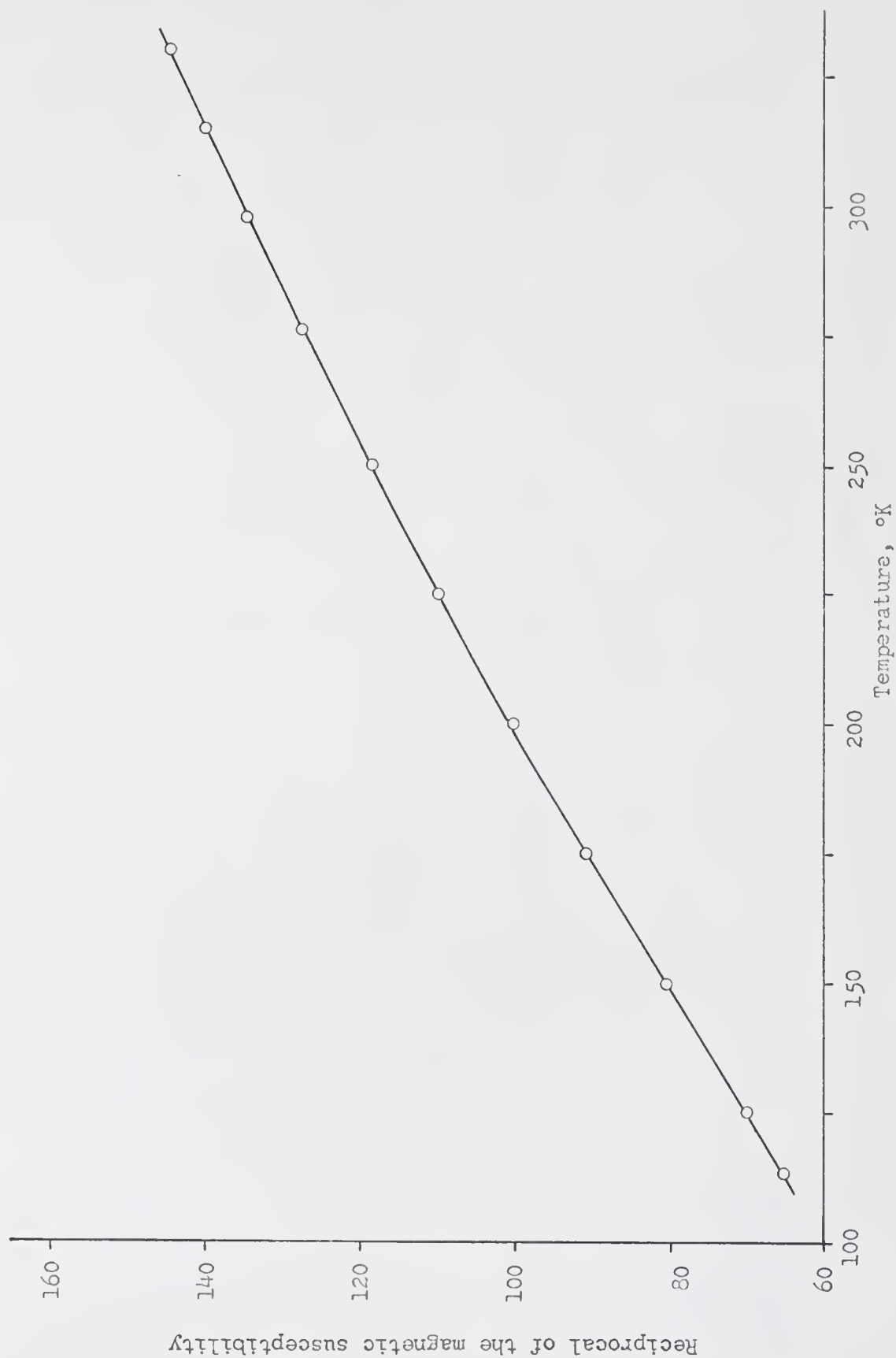


Fig. 18.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$

TABLE 11

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF  $[\text{Co(terpy)}_2](\text{ClO}_4)_2$  AND  $[\text{Co(terpy)}_2][\text{B(C}_6\text{H}_5)_4]_2$   
WITH TEMPERATURE

$[\text{Co(terpy)}_2](\text{ClO}_4)_2$				$[\text{Co(terpy)}_2][\text{B(C}_6\text{H}_5)_4]_2$			
T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\chi_c \times 10^6$	$\mu_{\text{eff}}$	T, °K	$\mu_{\text{eff}}$
114.88	5,631	2.28	113.87	15,343	3.75		
124.99	5,521	2.36	124.99	14,313	3.80		
149.98	5,536	2.59	149.97	12,432	3.88		
175.01	5,897	2.89	175.01	11,026	3.95		
199.99	6,409	3.22	199.99	10,010	4.02		
225.04	6,786	3.51	225.04	9,105	4.06		
250.01	6,971	3.75	250.01	8,466	4.13		
269.74	6,986	3.90	276.06	7,871	4.19		
296.44	6,856	4.05	297.94	7,445	4.23		
315.03	6,715	4.13	315.03	7,117	4.25		
334.98	6,550	4.21	330.03	6,913	4.29		

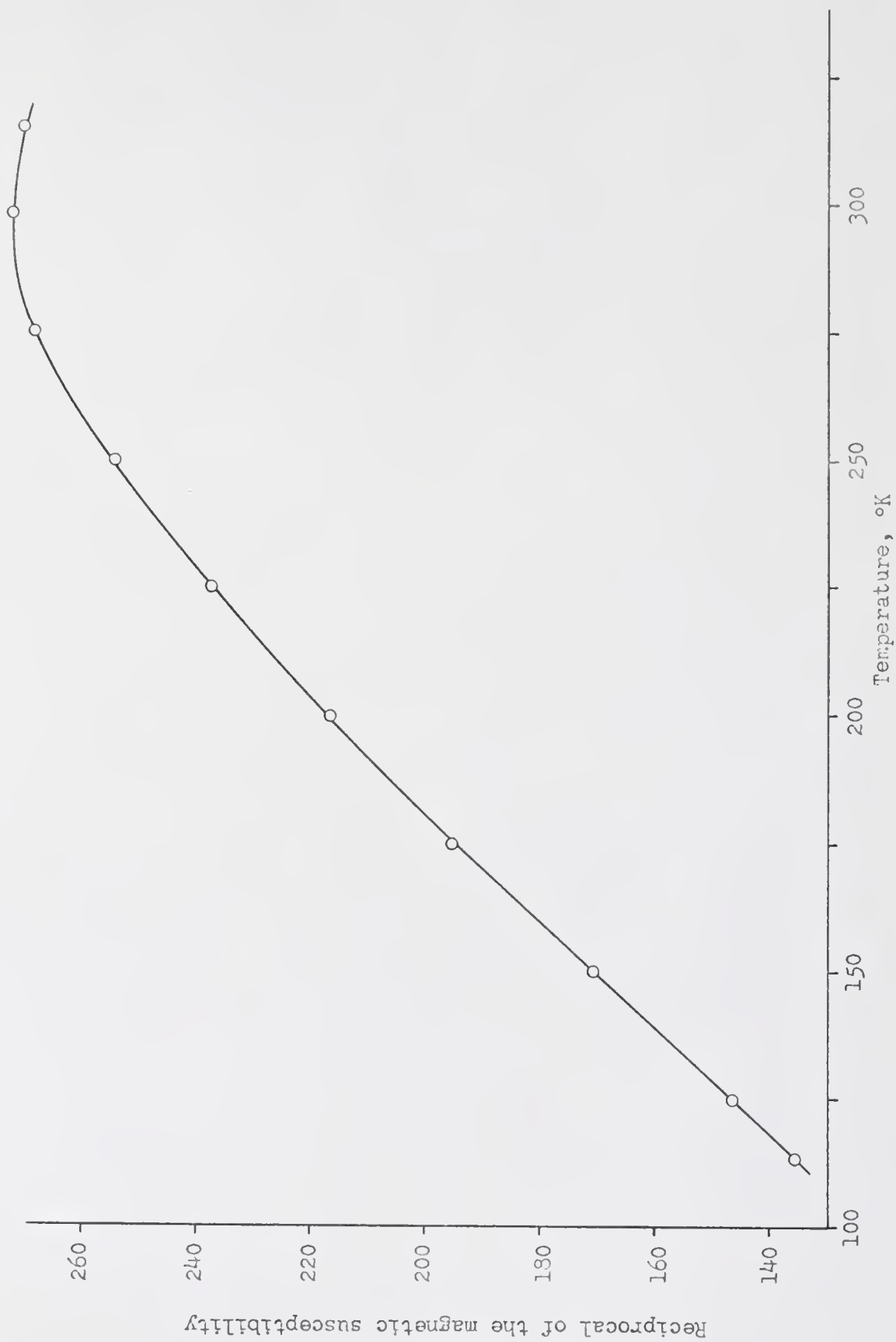


Fig. 19.- Temperature dependent susceptibility of  $[\text{Co}(\text{terpy})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$

TABLE 12  
VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
OF [Co(terpy)<sub>2</sub>]SO<sub>4</sub>·2H<sub>2</sub>O WITH TEMPERATURE

T	[Co(terpy) <sub>2</sub> ]SO <sub>4</sub> ·2H <sub>2</sub> O χ <sub>c</sub> x 10 <sup>6</sup>	μ <sub>eff</sub>
113.37	7,389	2.60
124.99	6,825	2.62
149.98	5,874	2.67
175.01	5,132	2.69
199.99	4,628	2.73
225.04	4,228	2.77
250.01	3,944	2.82
274.98	3,744	2.88
298.38	3,681	2.98
315.03	3,715	3.07

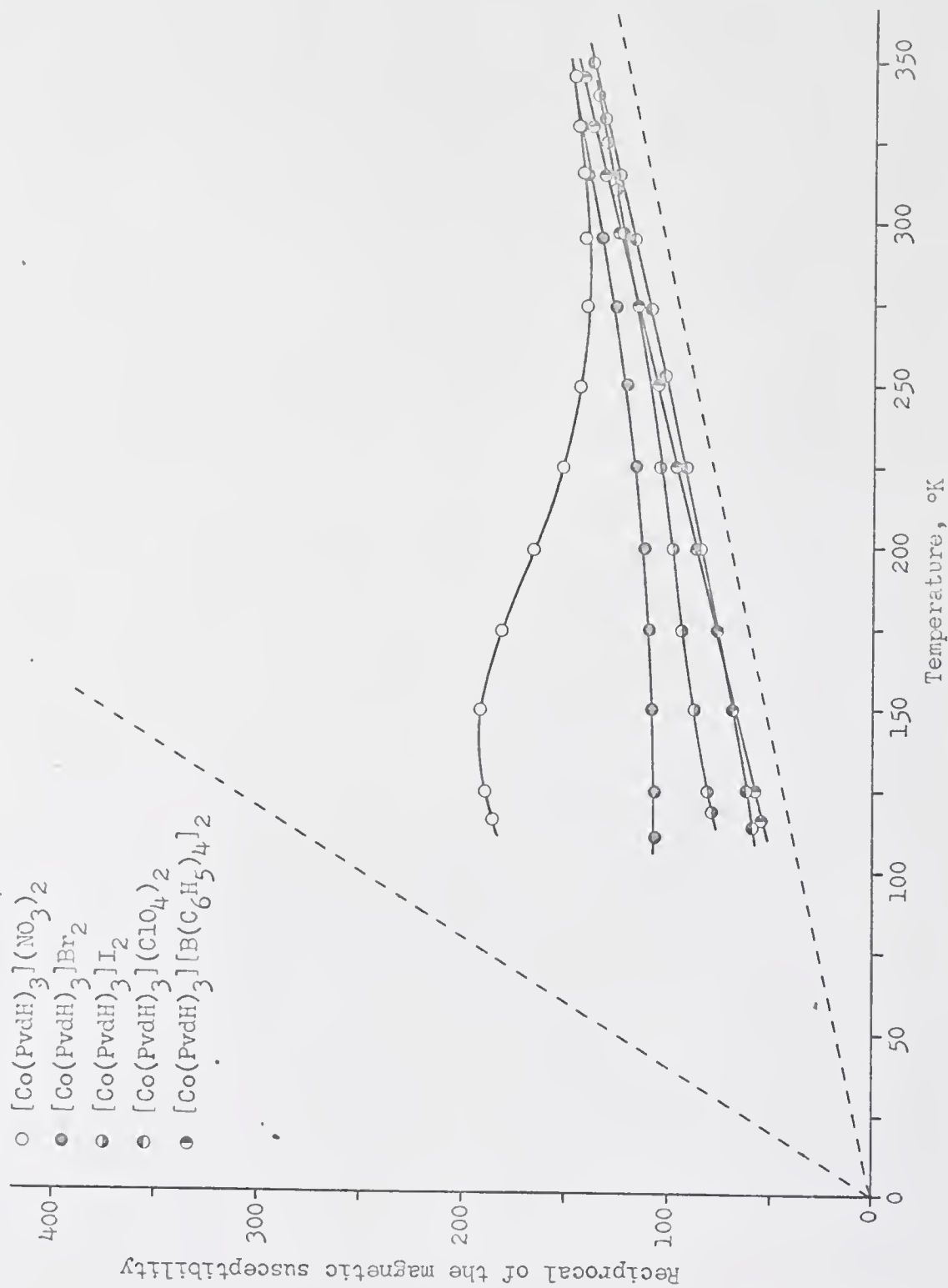


Fig. 20.- Temperature dependent susceptibilities of  $[\text{Co}(\text{PvdH})_3]^{2+}$  complexes

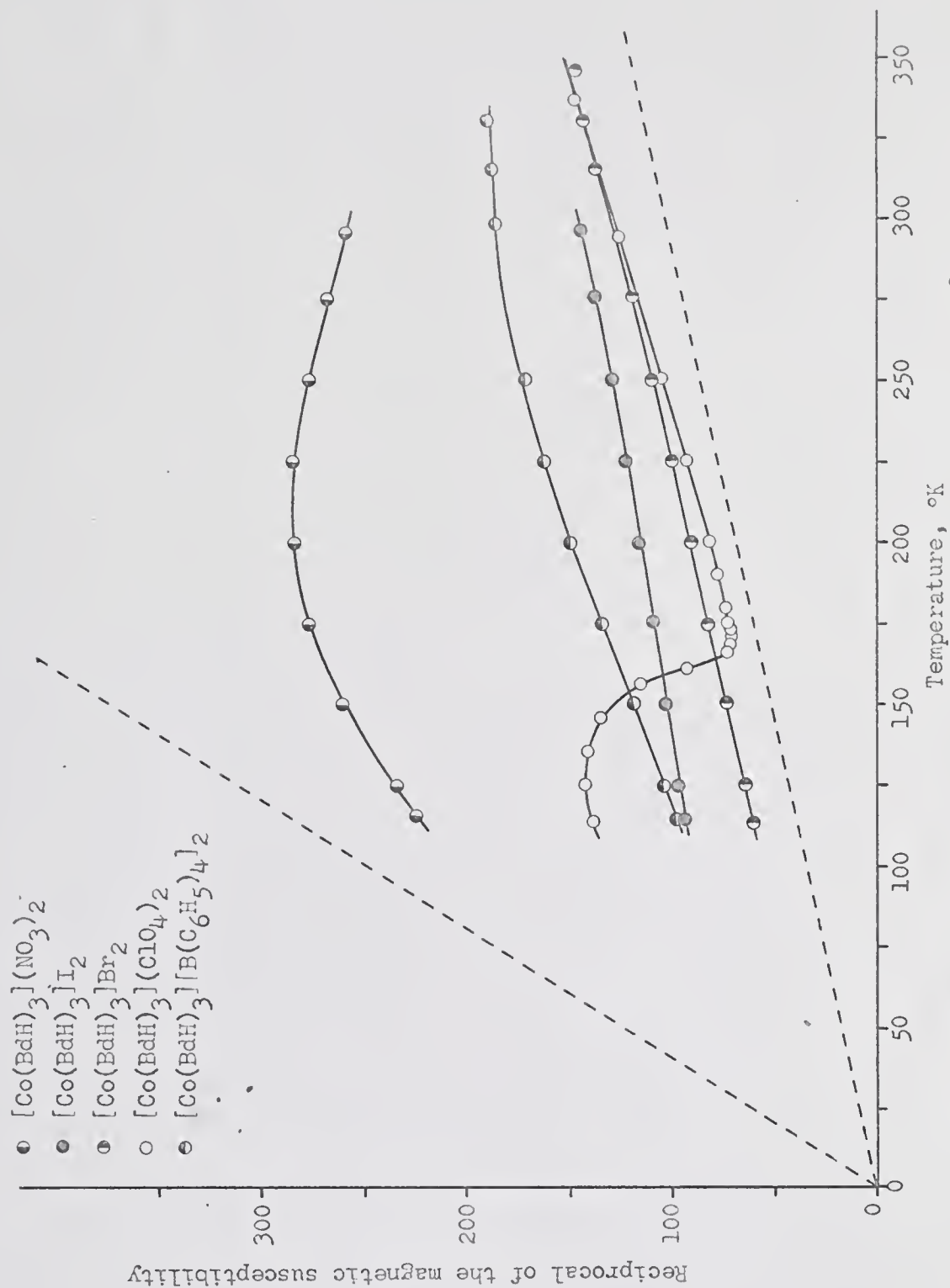


Fig. 21.- Temperature dependent susceptibilities of  $[\text{Co}(\text{BdH})_3]^{2+}$  complexes

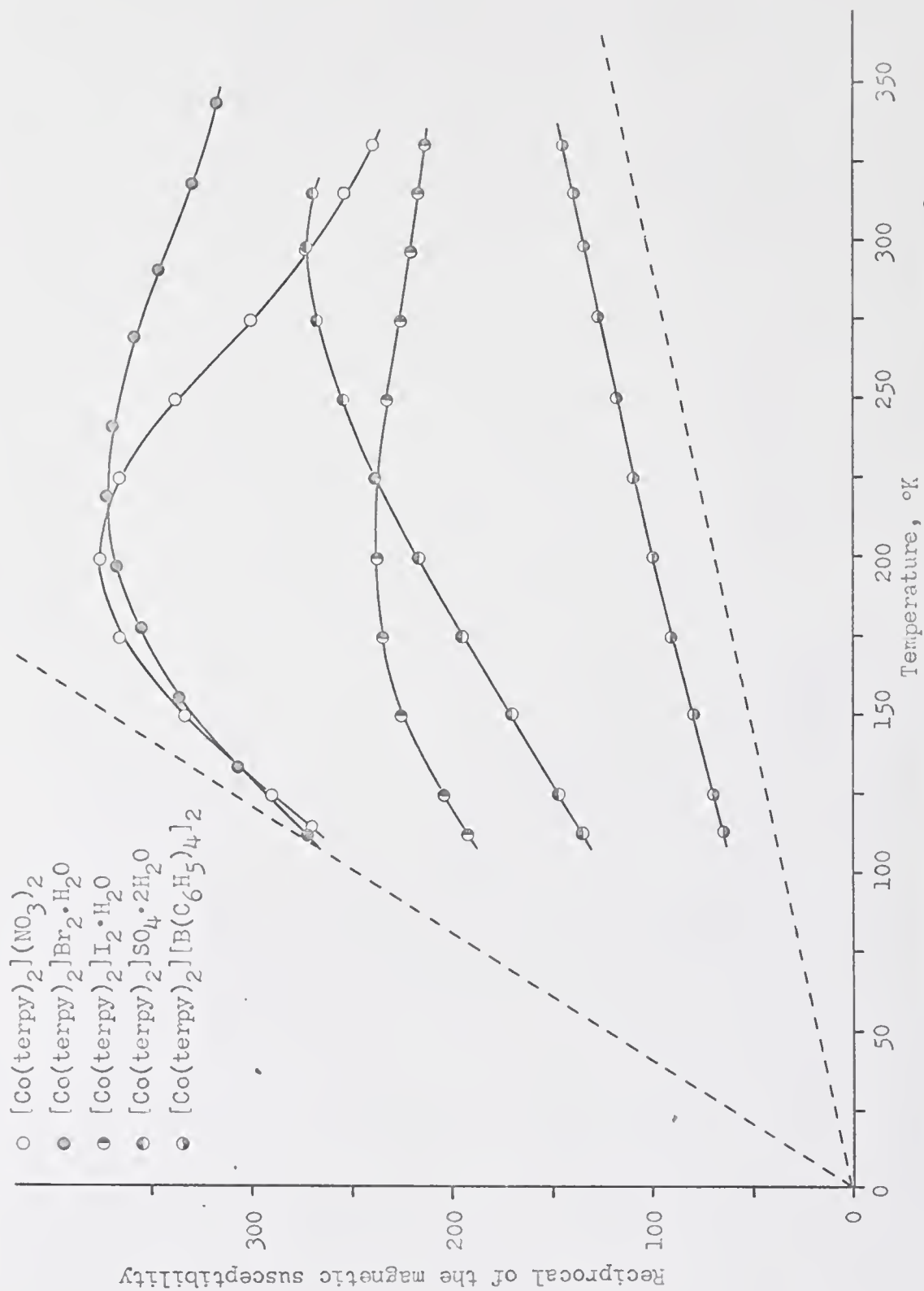


Fig. 22.- Temperature dependent susceptibilities of some  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes

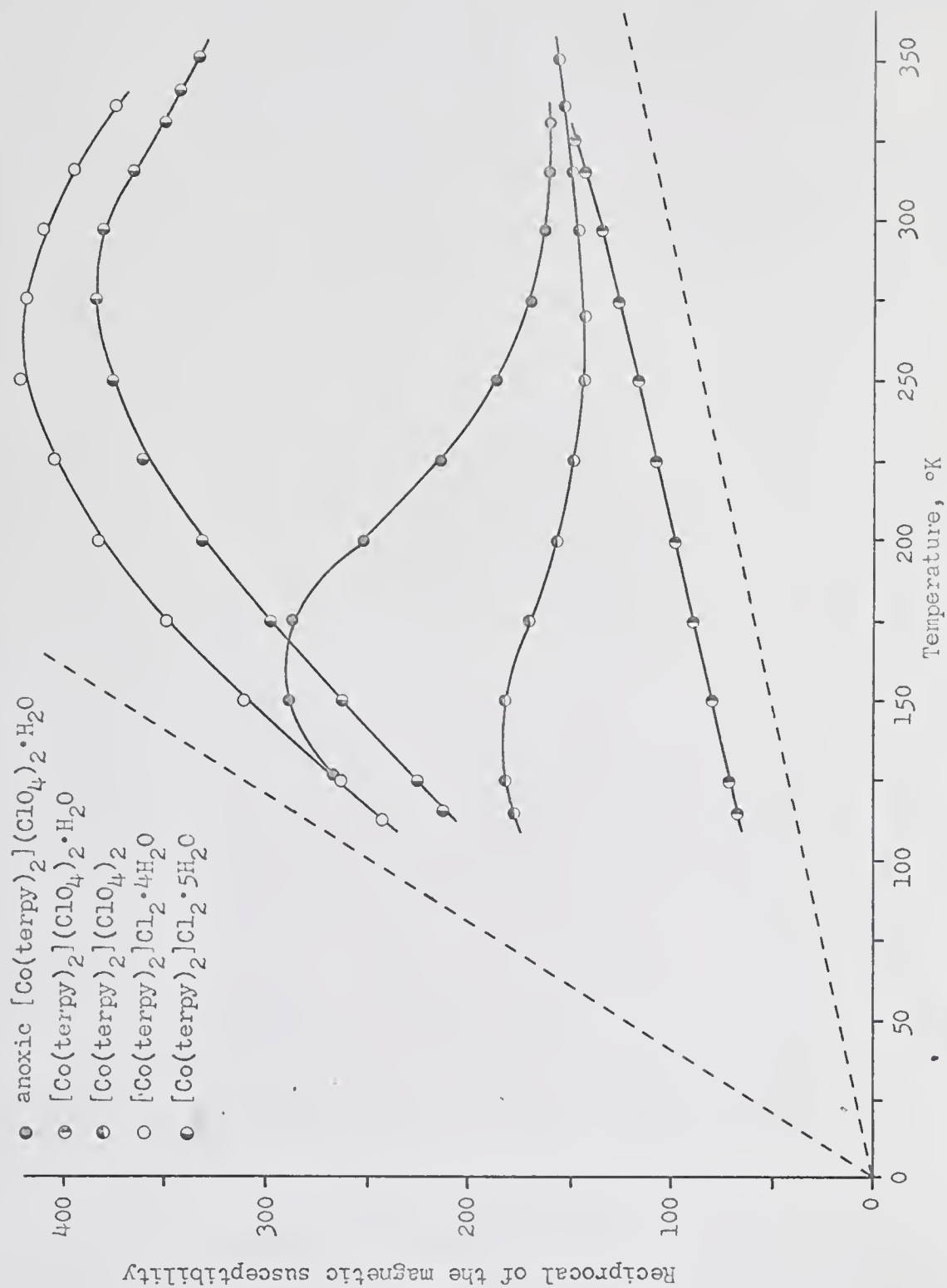


Fig. 23.-- Temperature dependent susceptibilities of remaining  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes



corresponding to temperature-independent magnetic moments of 4.9 B.M. (lower line) and 1.9 B.M. (upper line). Only one compound,  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  with a Weiss constant of  $26^\circ$ , obeys the Curie-Weiss law over the entire temperature range studied. Two compounds,  $[\text{Co}(\text{BdH})_3]\text{I}_2$  and  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , have been reported previously to follow the Curie-Weiss law exhibiting rather high values of the Weiss constant of  $142^\circ$  and  $65^\circ$ , respectively (55). However, the present investigation indicates that although Curie-Weiss behavior is normal over a portion of each of the curves, deviations occur at the upper temperatures. This was detected by taking a greater number of measurements over smaller temperature intervals.

In addition, the data here differ in part with those reported by Hogg and Wilkins (34) on  $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ . The general shape of the  $1/\chi$  versus  $T$  curves are similar, but the values of the susceptibility reported are inconsistent within themselves in that the text data do not agree with the listed data. There are other obvious errors in the article (34).

Some differences in experimental values should not be unexpected, however, in view of the extreme sensitivity of the magnetic moment of anomalous complexes to the crystal lattice (see Discussion). It has been reported previously that small differences in the procedure of preparation can be very important on the magnetic behavior (4).

The graphical presentations of the magnetic moments as a function of temperature in Figures 24 through 27 illustrate the fact that none of the magnetic moments falls below the low-spin octahedral cobalt(II) range nor above the high-spin octahedral cobalt(II) range. All of the magnetic moments are dependent upon the temperature.

It is interesting to note in Table 2 that the moments of  $[\text{Co}(\text{PvdH})_3]^{2+}$ ,  $[\text{Co}(\text{BdH})_3]^{2+}$ , and  $[\text{Co}(\text{terpy})_2]^{2+}$  in solution are  $4.77 \pm 0.10$ ,  $4.60 \pm 0.10$ , and  $3.35 \pm 0.15$  B.M., respectively. It was assumed that dissolving a complex in a suitable solvent would remove any effects of the solid state and the anion, if such effects were present. In that the magnetic moments of identical cations in solution are the same within experimental error, the assumption was a valid one. The solution magnetic moments are therefore used as reference standards from which deviations in the solid state can be based.

### X-Ray Diffraction Measurements

The X-ray diffraction patterns of compounds prepared during the course of this investigation are illustrated graphically in Figures 28 through 46. One compound, anoxic  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , could not be kept sufficiently free of oxygen for its diffraction pattern to be obtained. For a single complex at a given temperature the peak of greatest

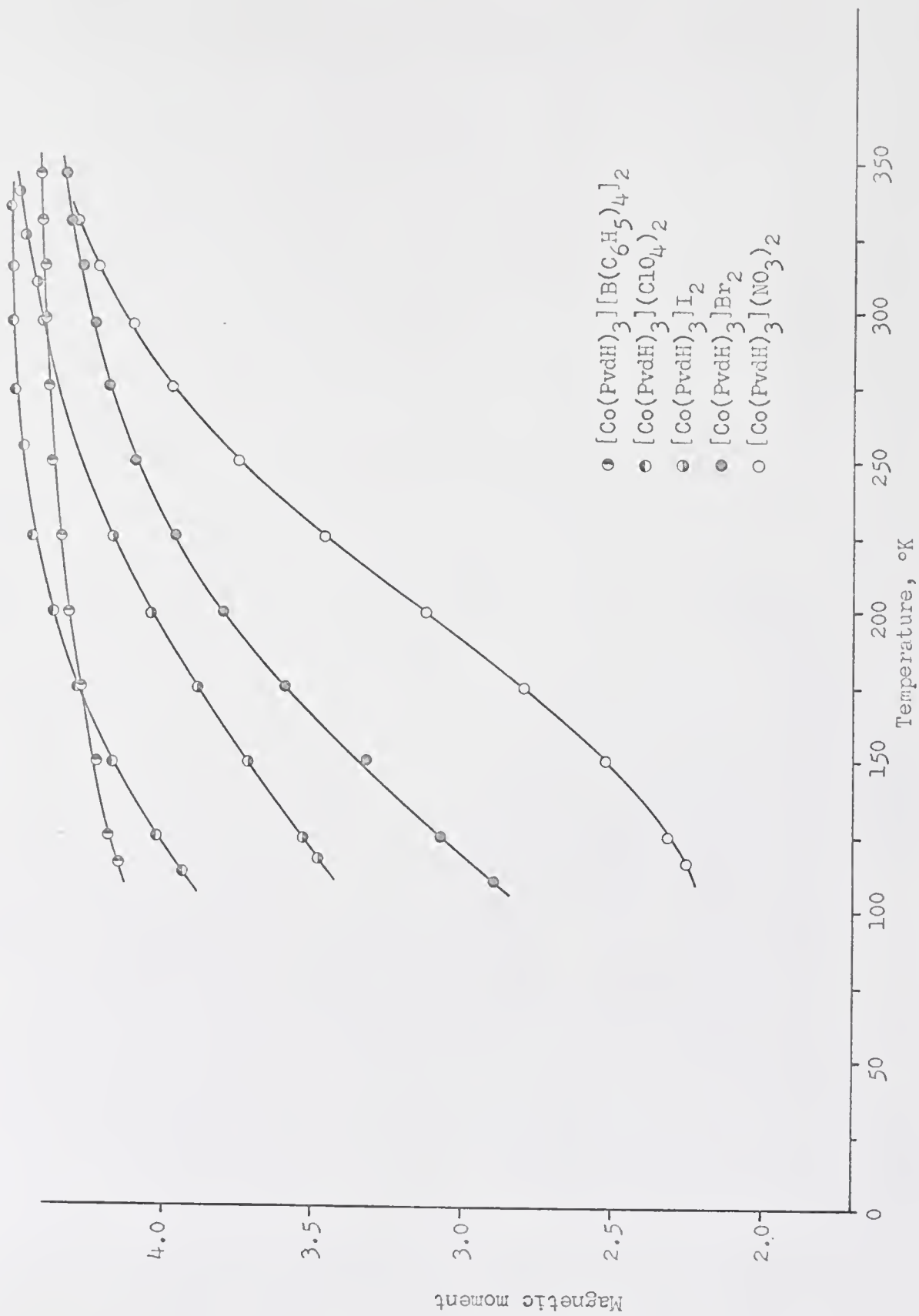


Fig. 24.- Temperature dependent magnetic moments of  $[\text{Co}(\text{PvdH})_3]^{2+}$  complexes

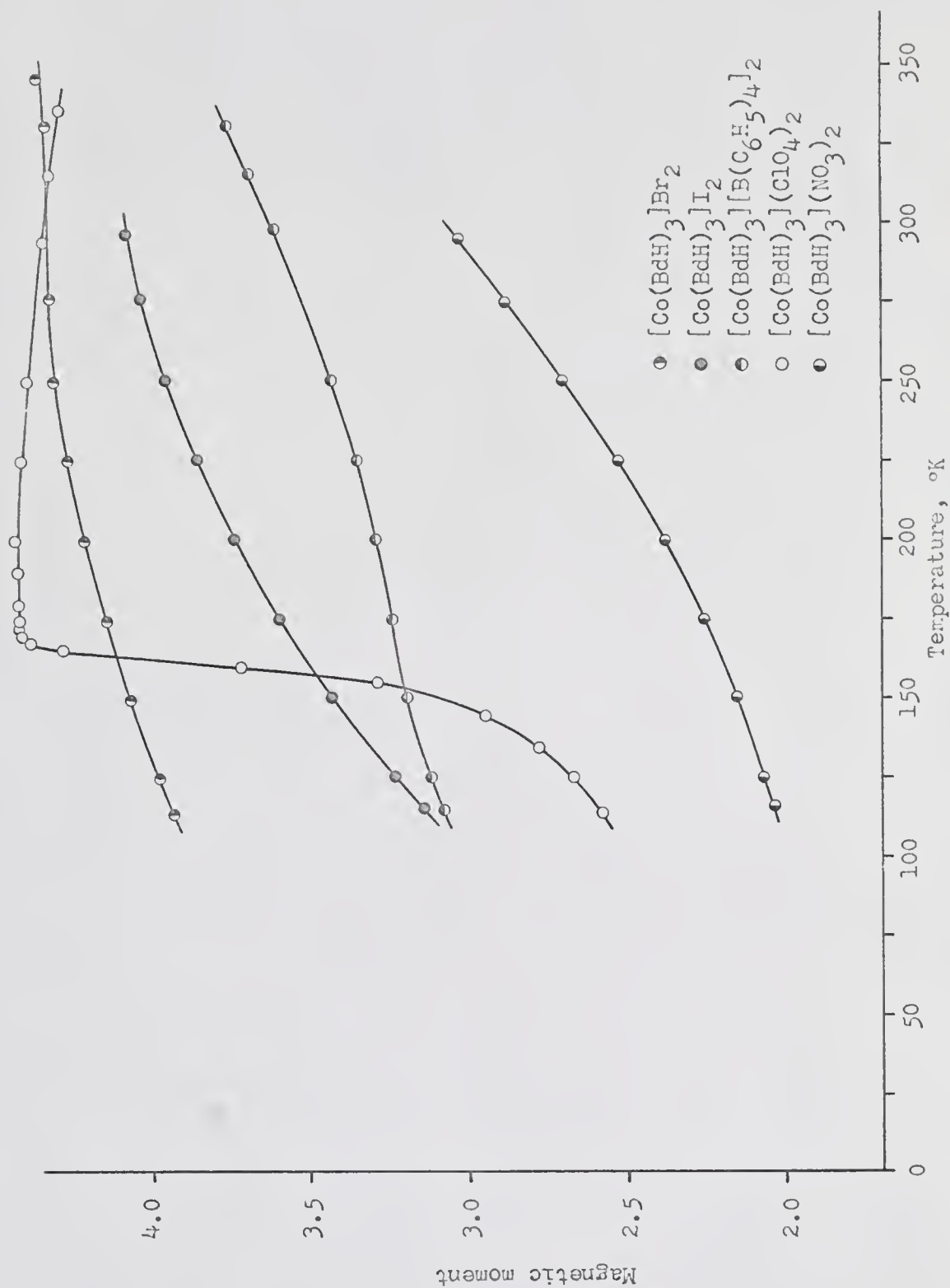


Fig. 25.- Temperature dependent magnetic moments of  $[\text{Co}(\text{BdH})_3]^{2+}$  complexes

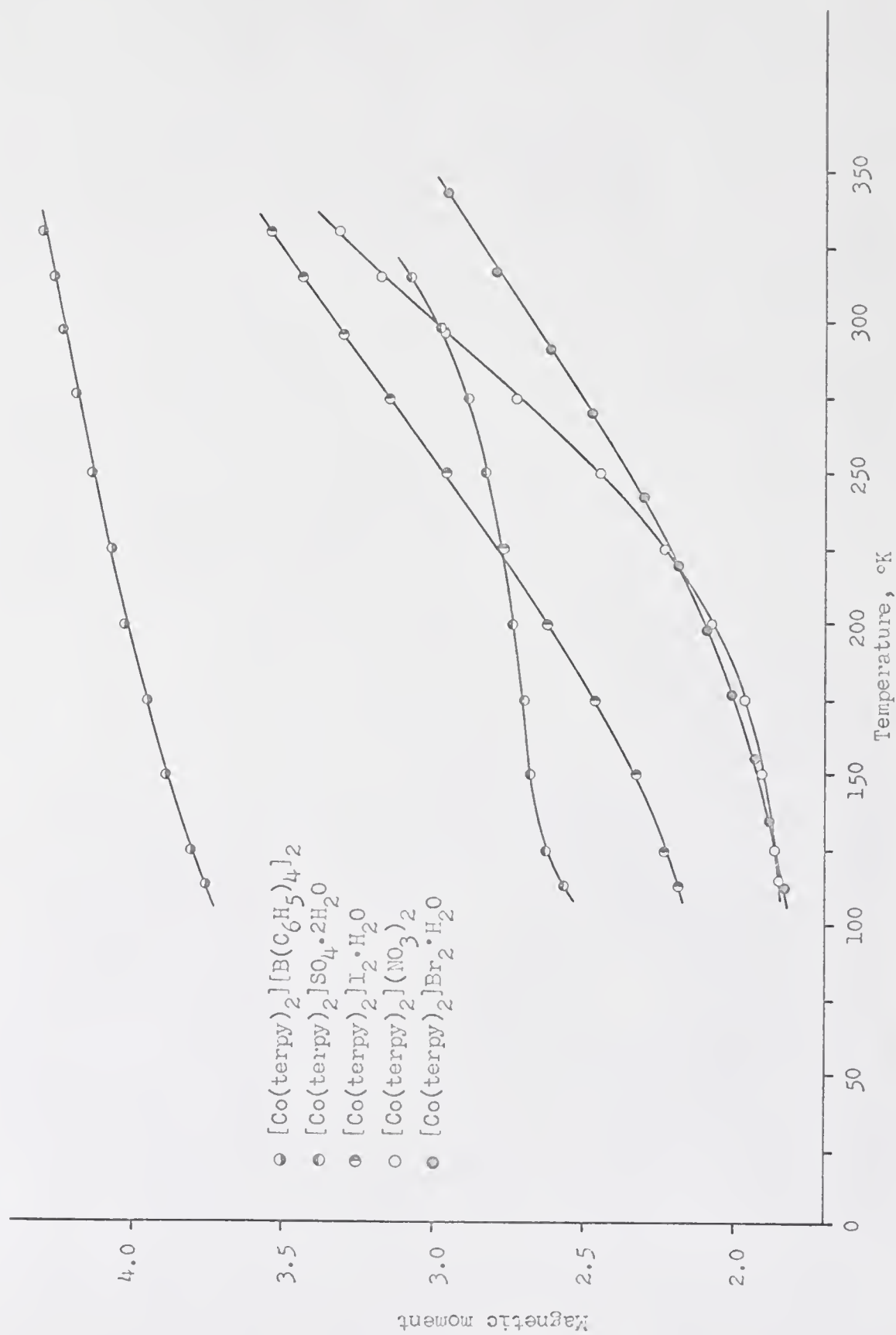


Fig. 26.- Temperature dependent magnetic moments of some  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes

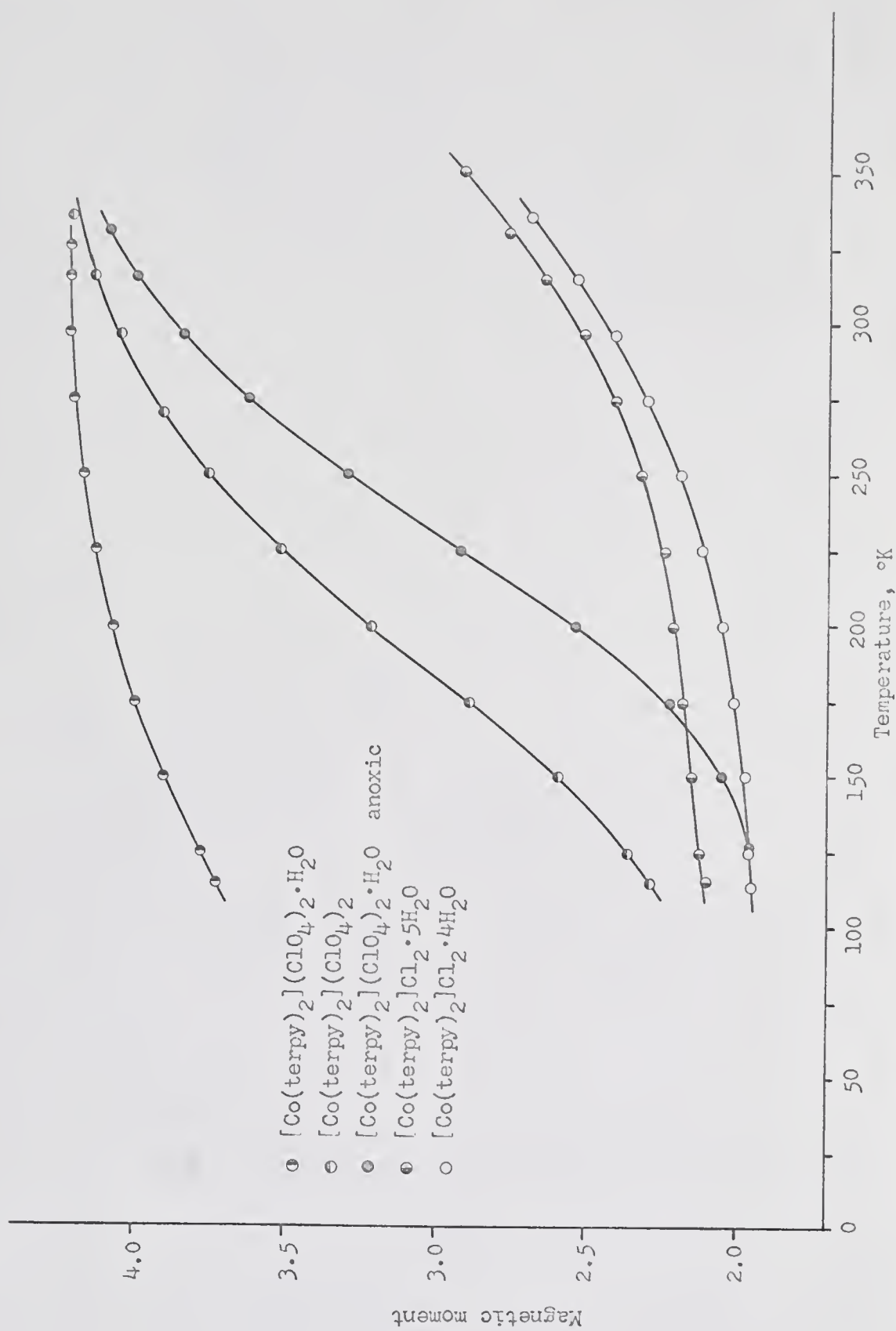


Fig. 27.- Temperature dependent magnetic moments of remaining  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes

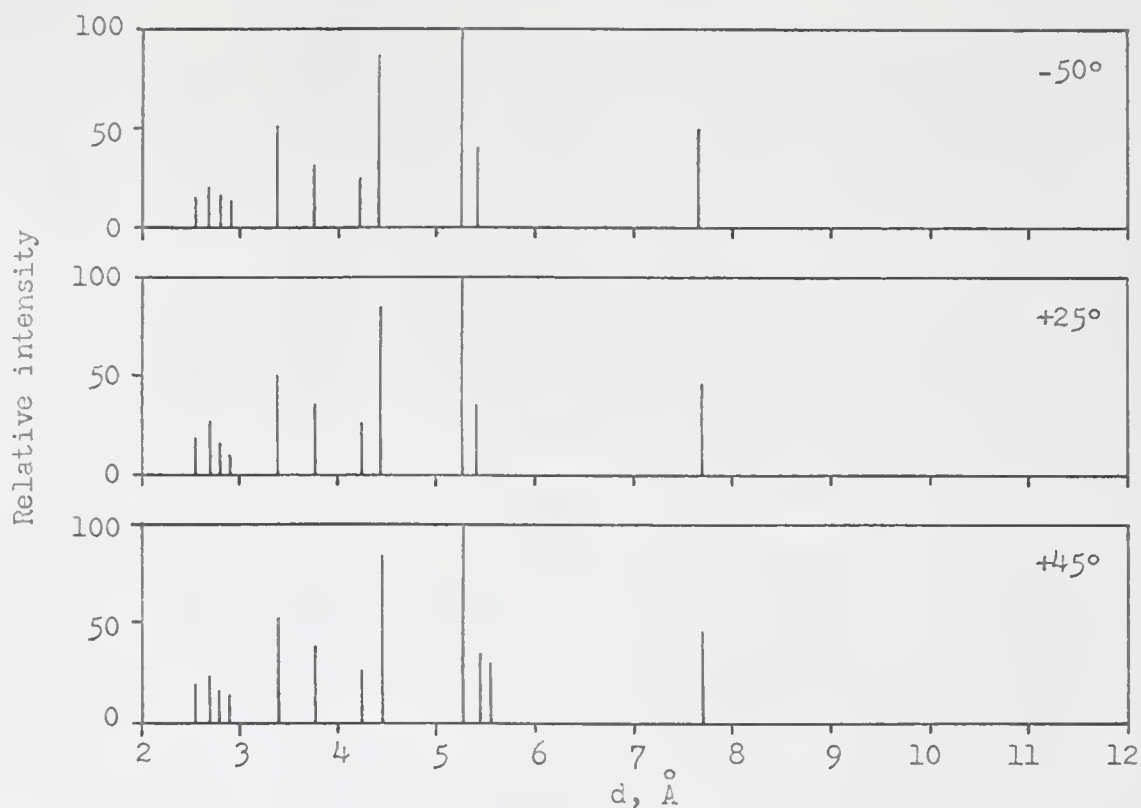


Fig. 28.- X-ray diffraction pattern of  $[\text{Co}(\text{PvdH})_3]\text{Br}_2$  at three temperatures

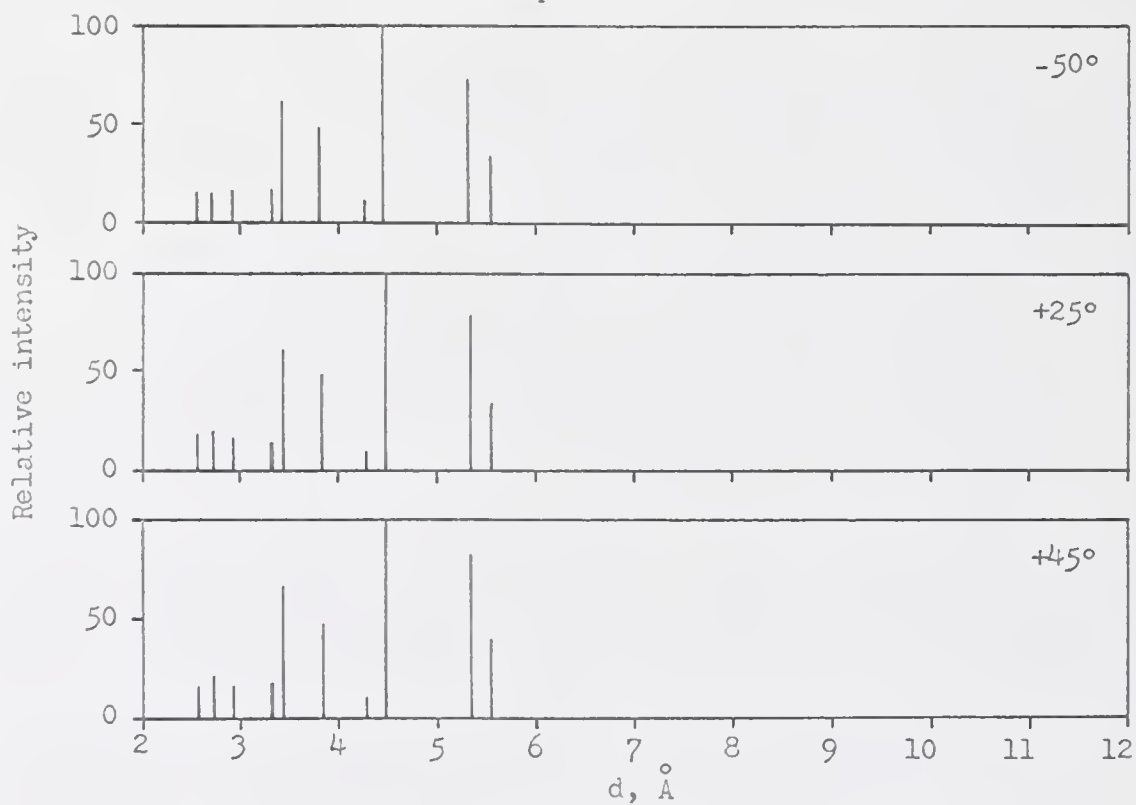


Fig. 29.- X-ray diffraction pattern of  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  at three temperatures

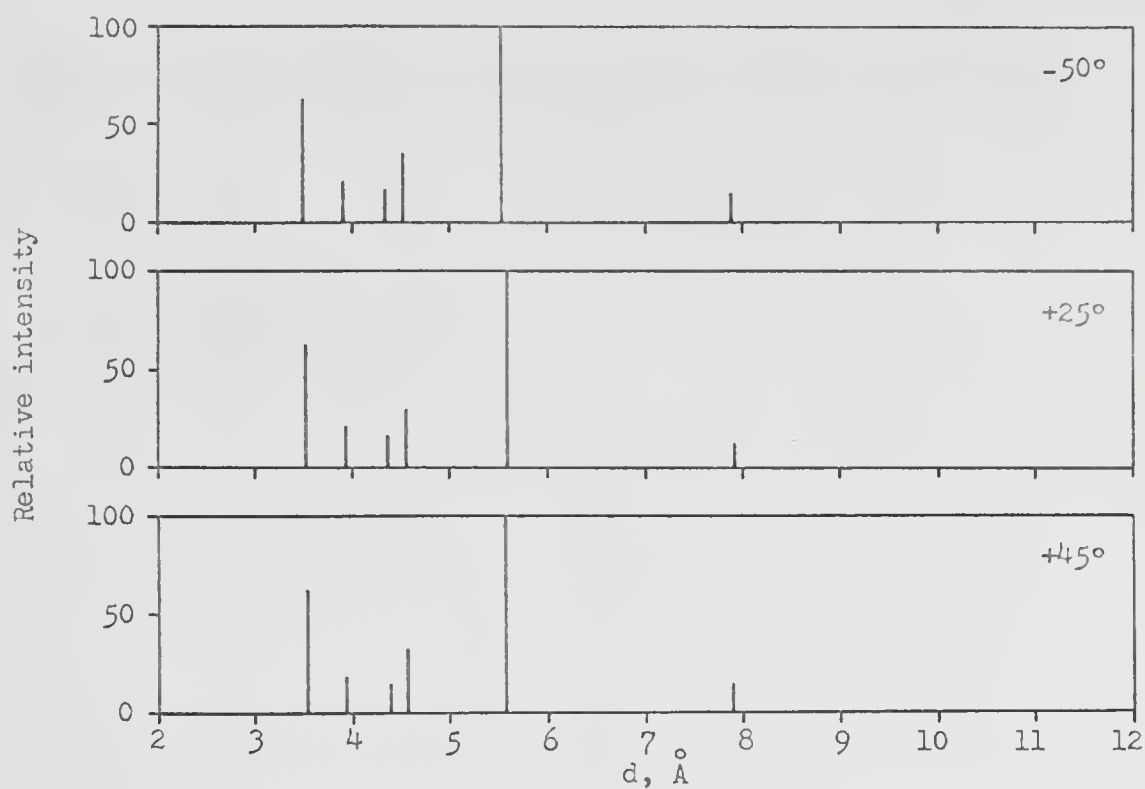


Fig. 30.- X-ray diffraction pattern of  $[\text{Co}(\text{PvdH})_3](\text{ClO}_4)_2$  at three temperatures

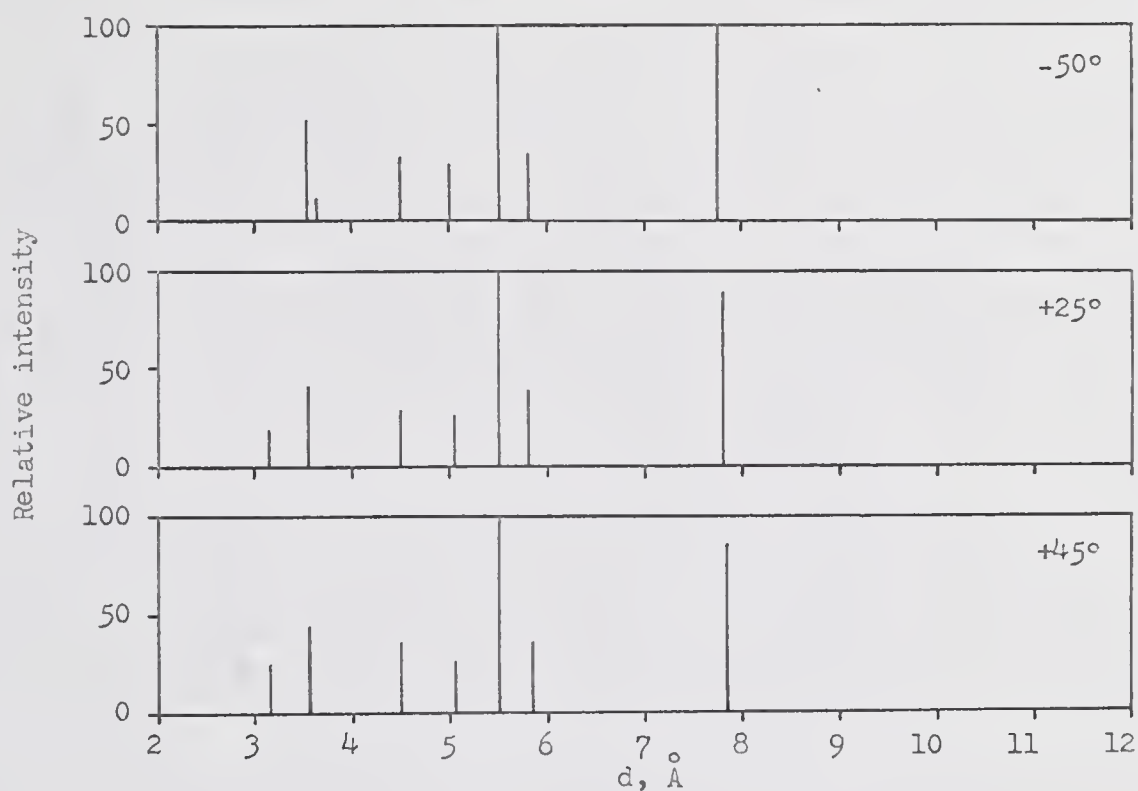


Fig. 31.- X-ray diffraction pattern of  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$  at three temperatures.



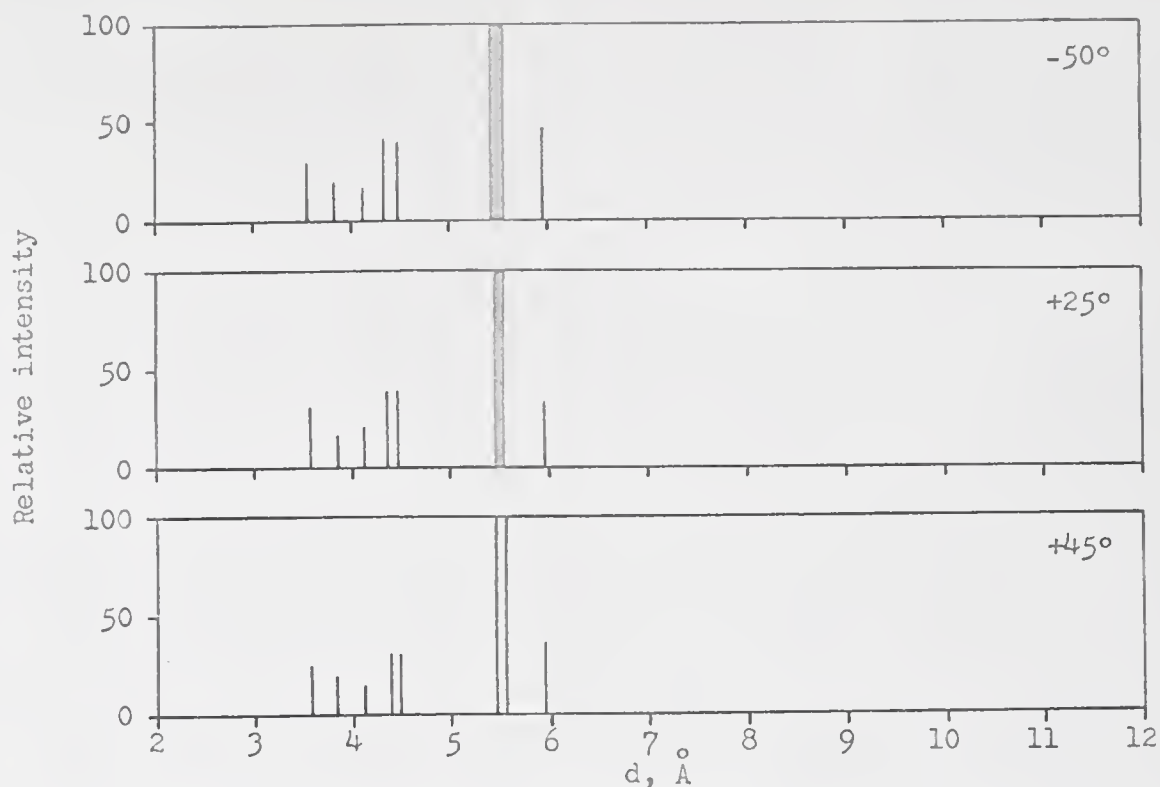


Fig. 32.- X-ray diffraction pattern of  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  at three temperatures

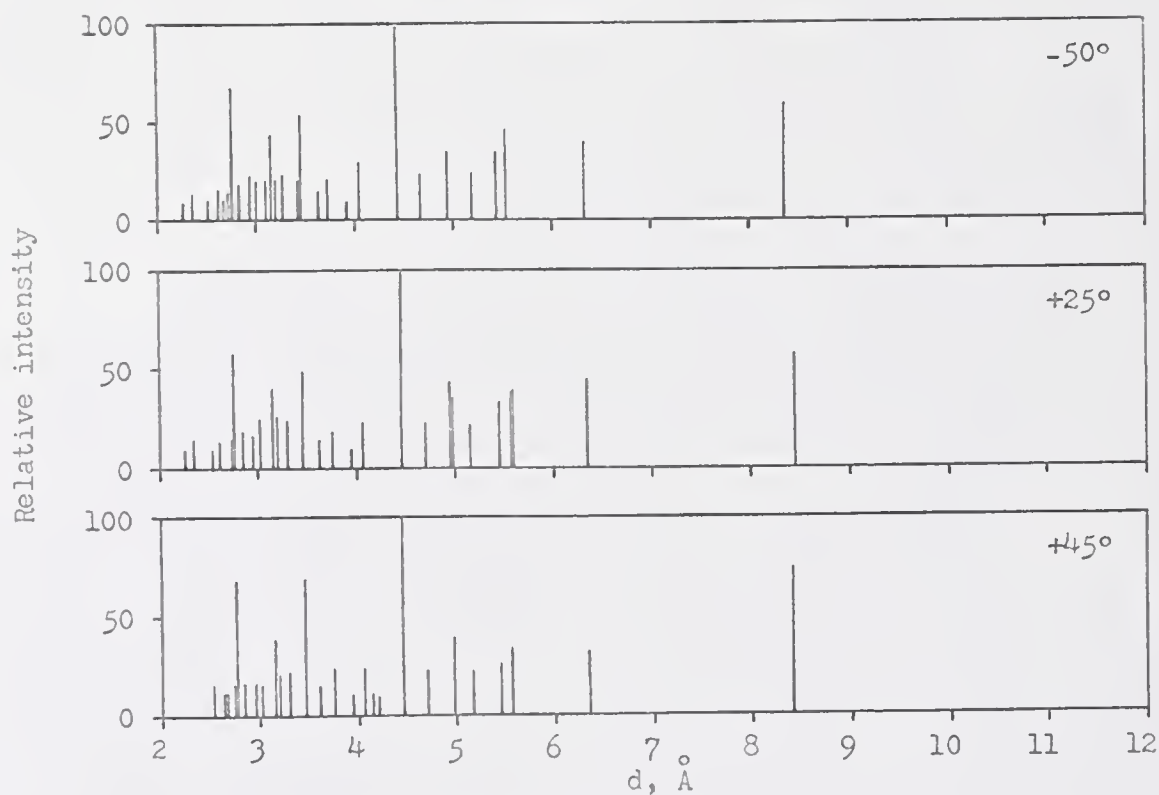


Fig. 33.- X-ray diffraction pattern of  $[\text{Co}(\text{BdH})_3]\text{Br}_2$  at three temperatures

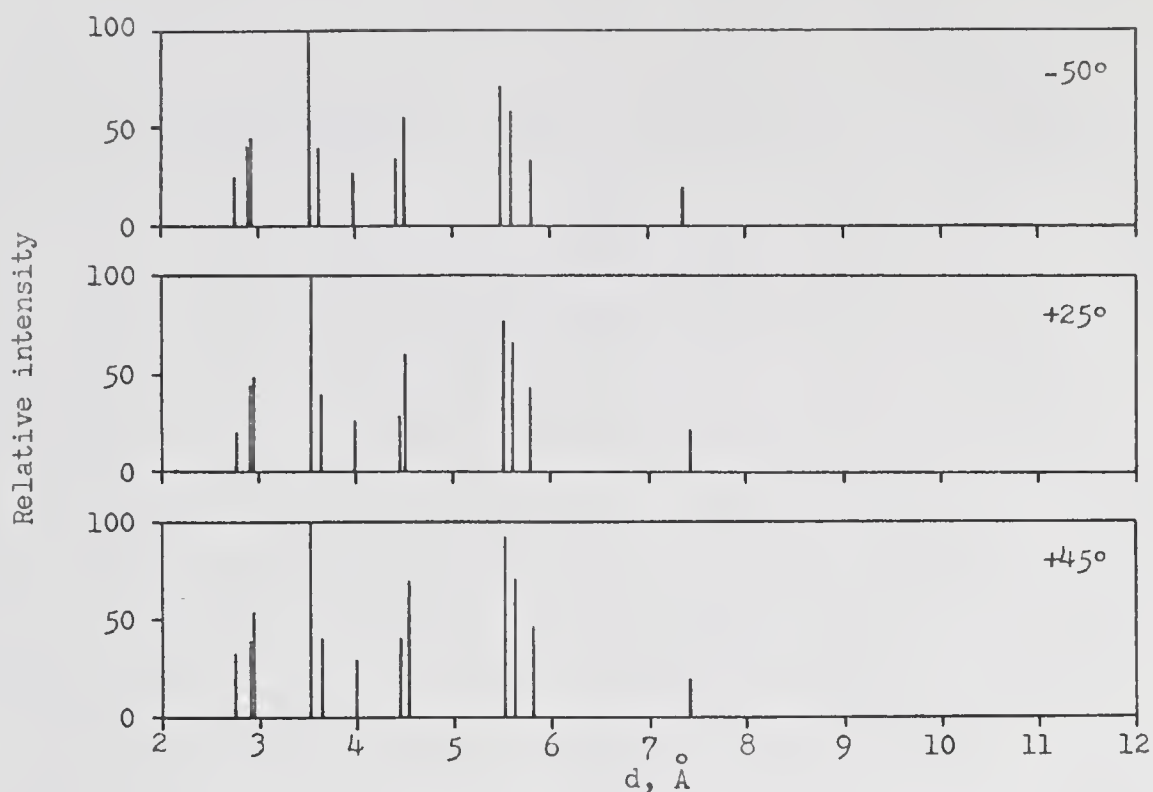


Fig. 34.- X-ray diffraction pattern of  $[\text{Co}(\text{BdH})_3]\text{I}_2$  at three temperatures

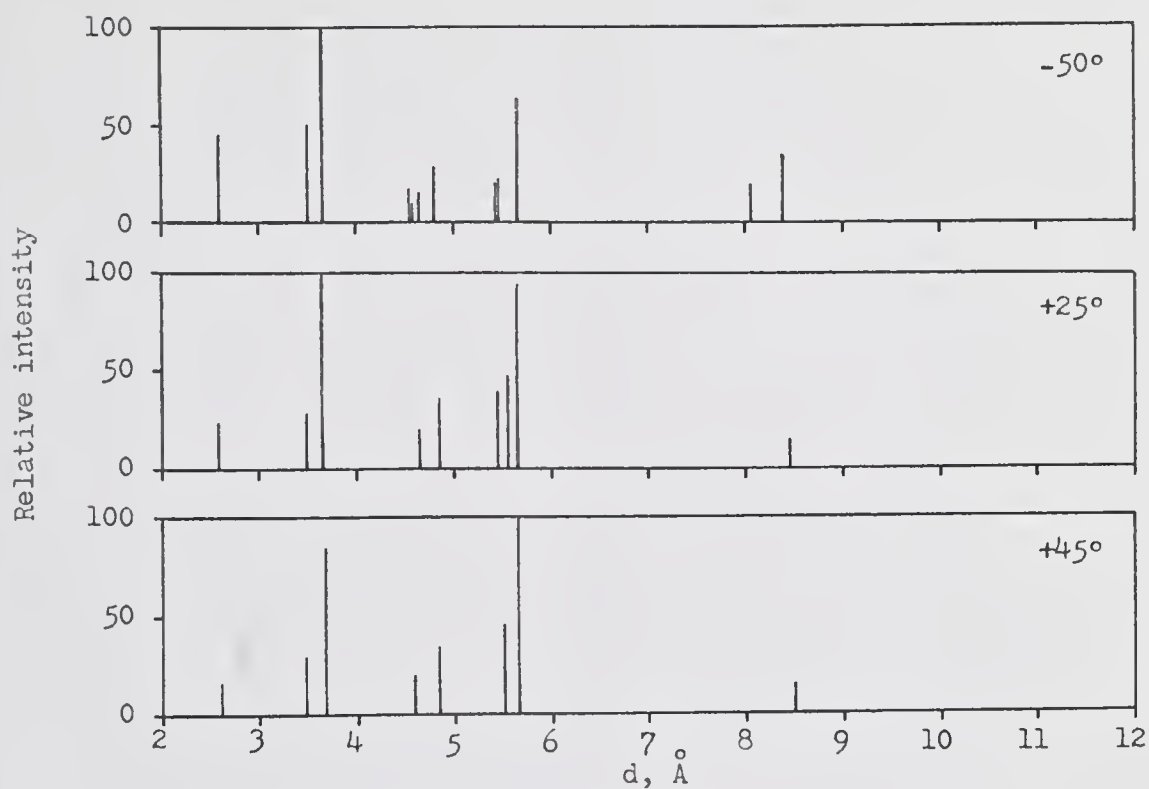


Fig. 35.- X-ray diffraction pattern of  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$  at three temperatures

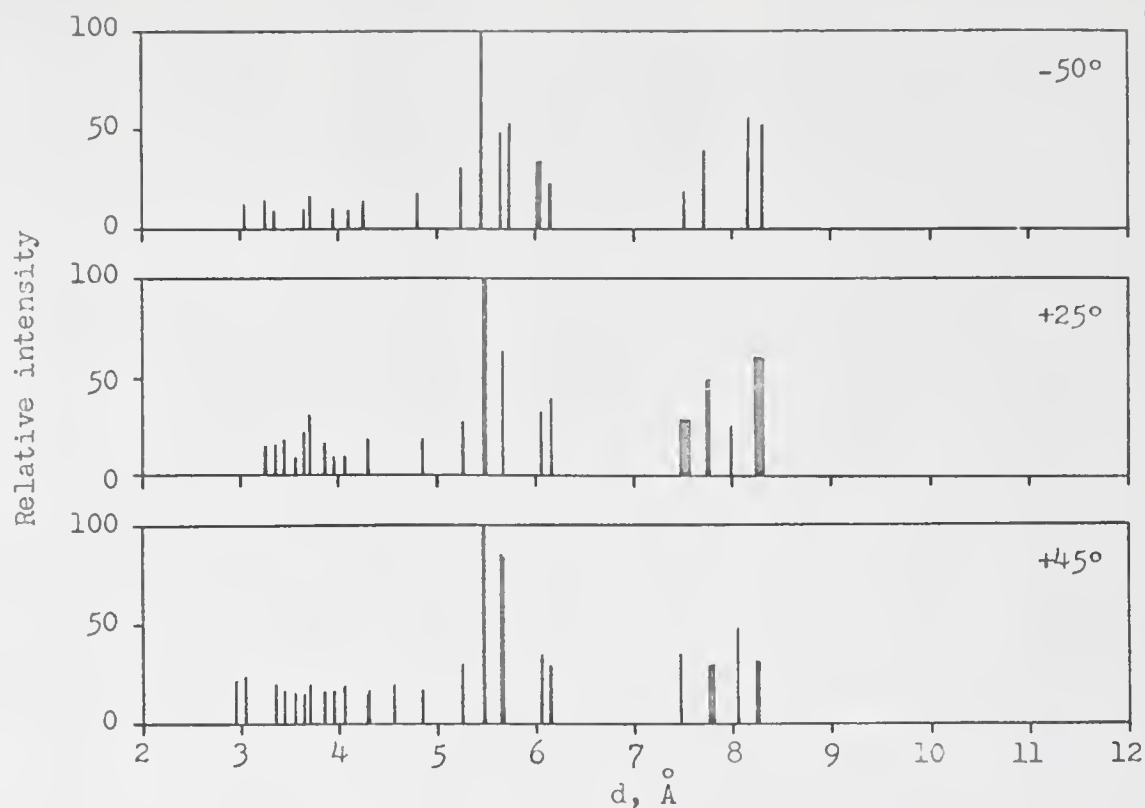


Fig. 36.- X-ray diffraction pattern of  $[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$  at three temperatures

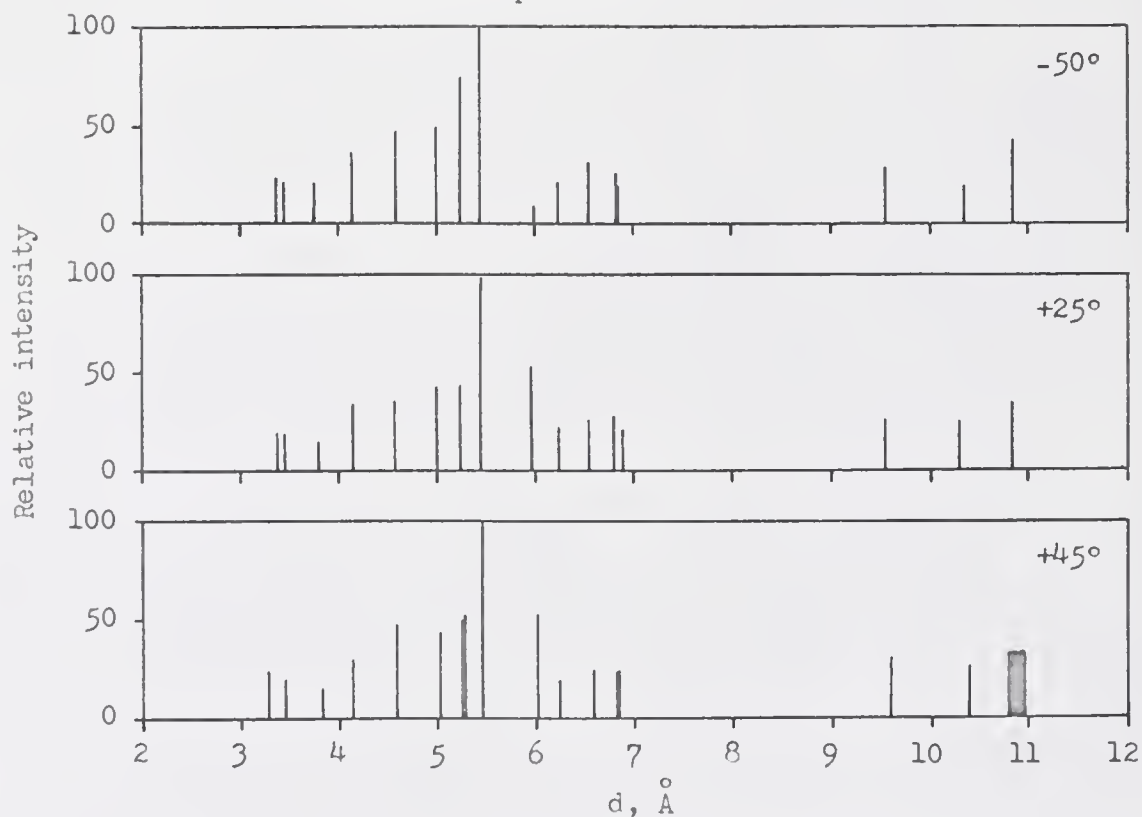


Fig. 37.- X-ray diffraction pattern of  $[\text{Co}(\text{BdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  at three temperatures

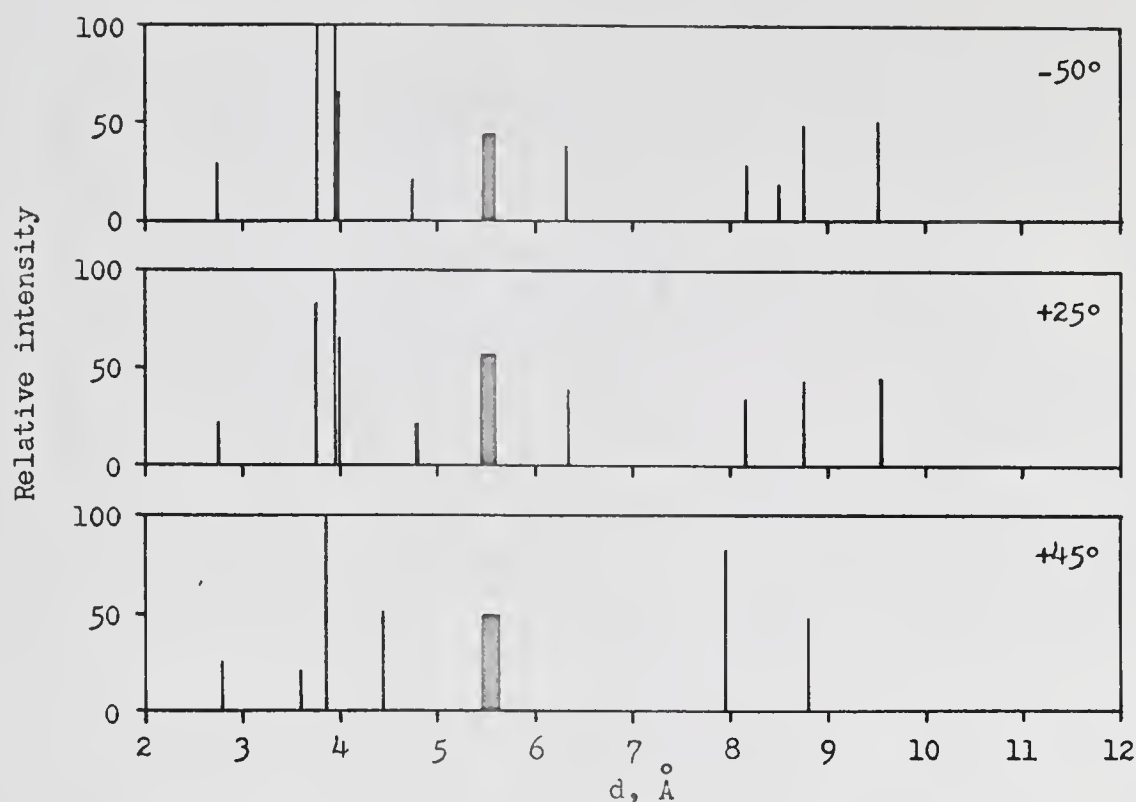


Fig. 38.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  at three temperatures

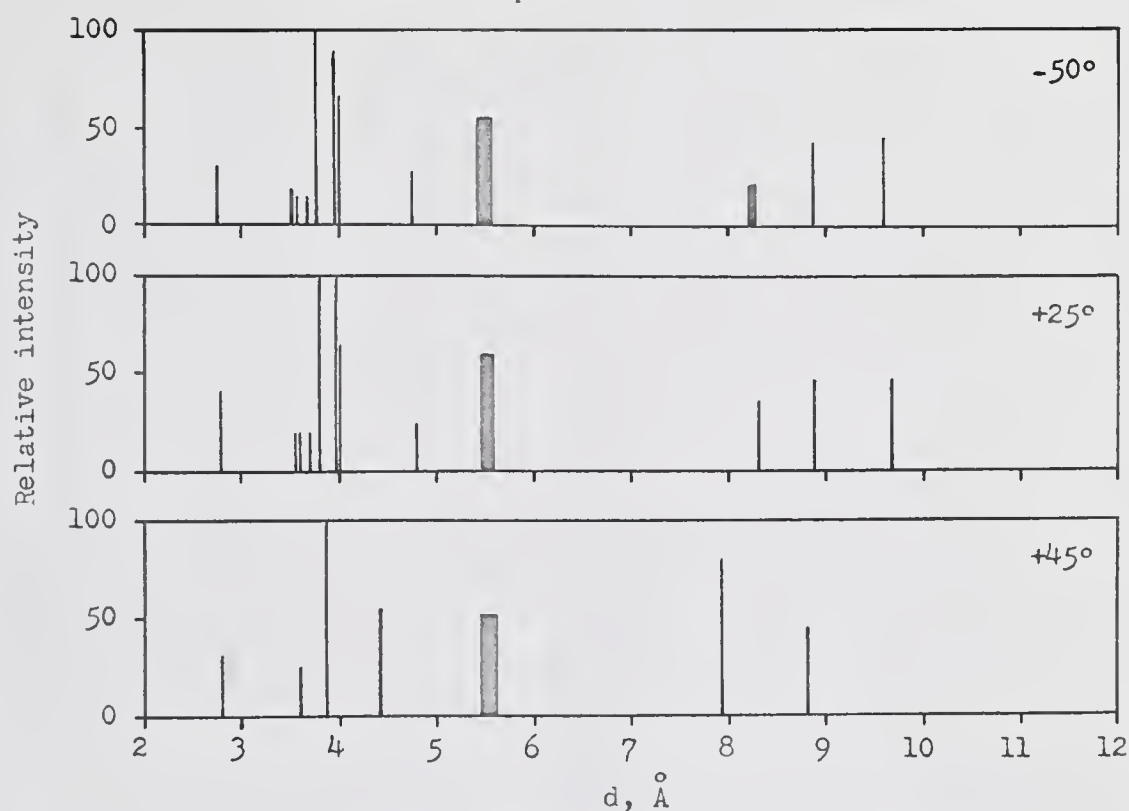


Fig. 39.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  at three temperatures

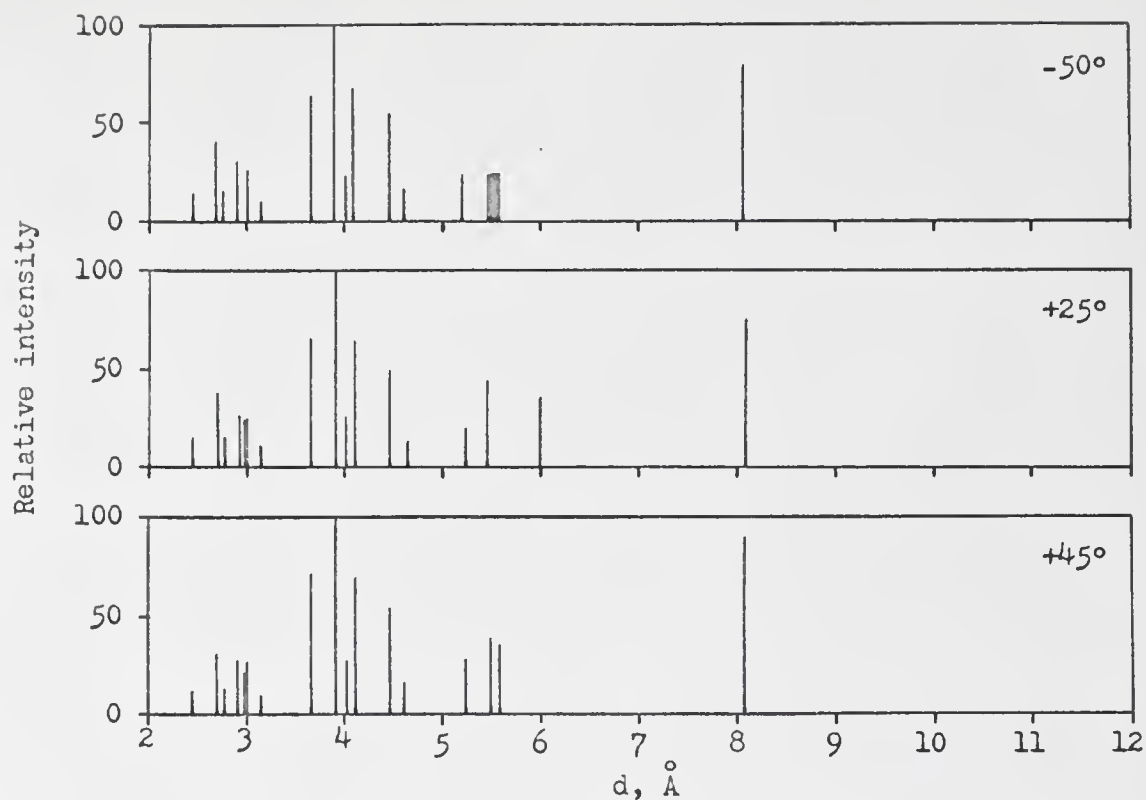


Fig. 40.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$  at three temperatures

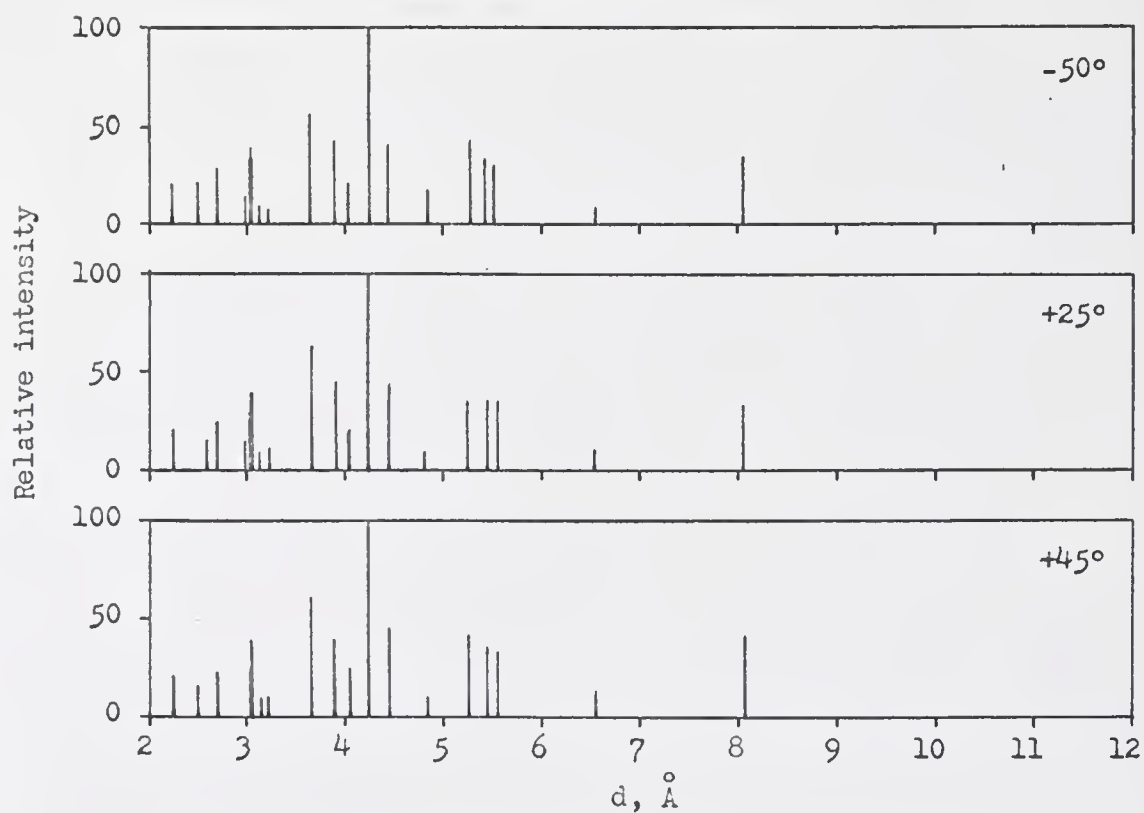


Fig. 41.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2]\text{I}_2 \cdot \text{H}_2\text{O}$  at three temperatures

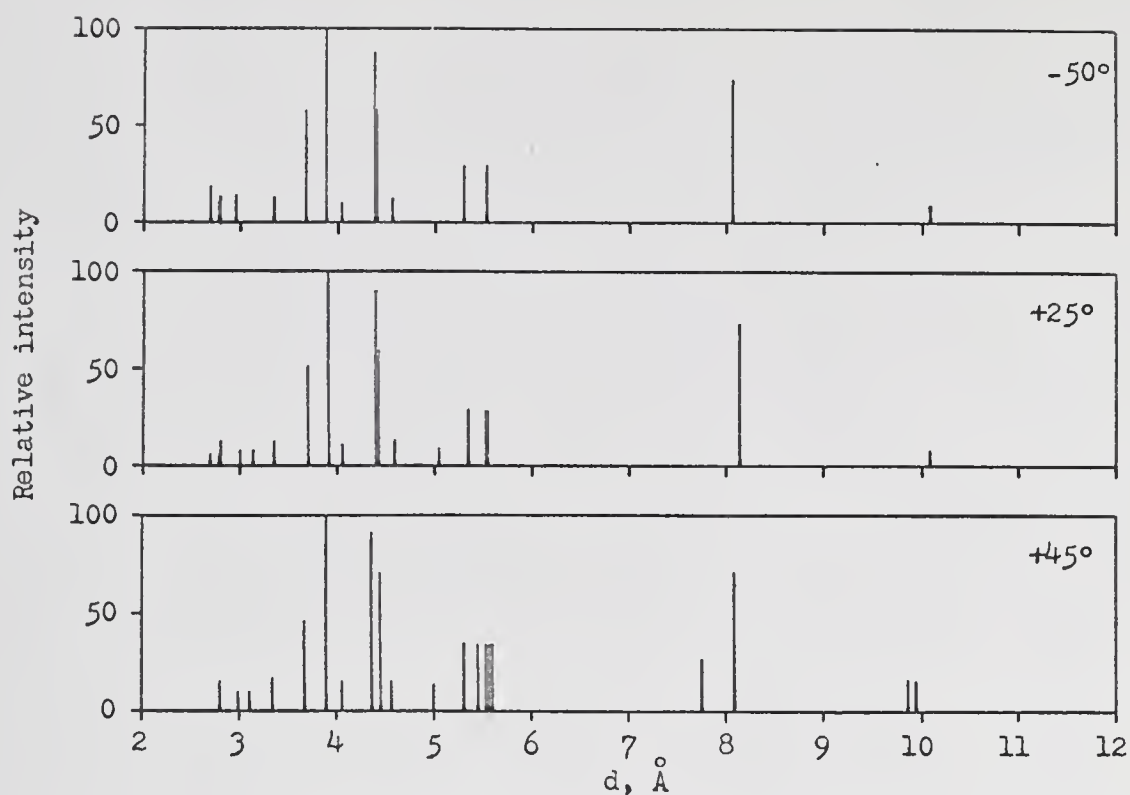


Fig. 42.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  at three temperatures

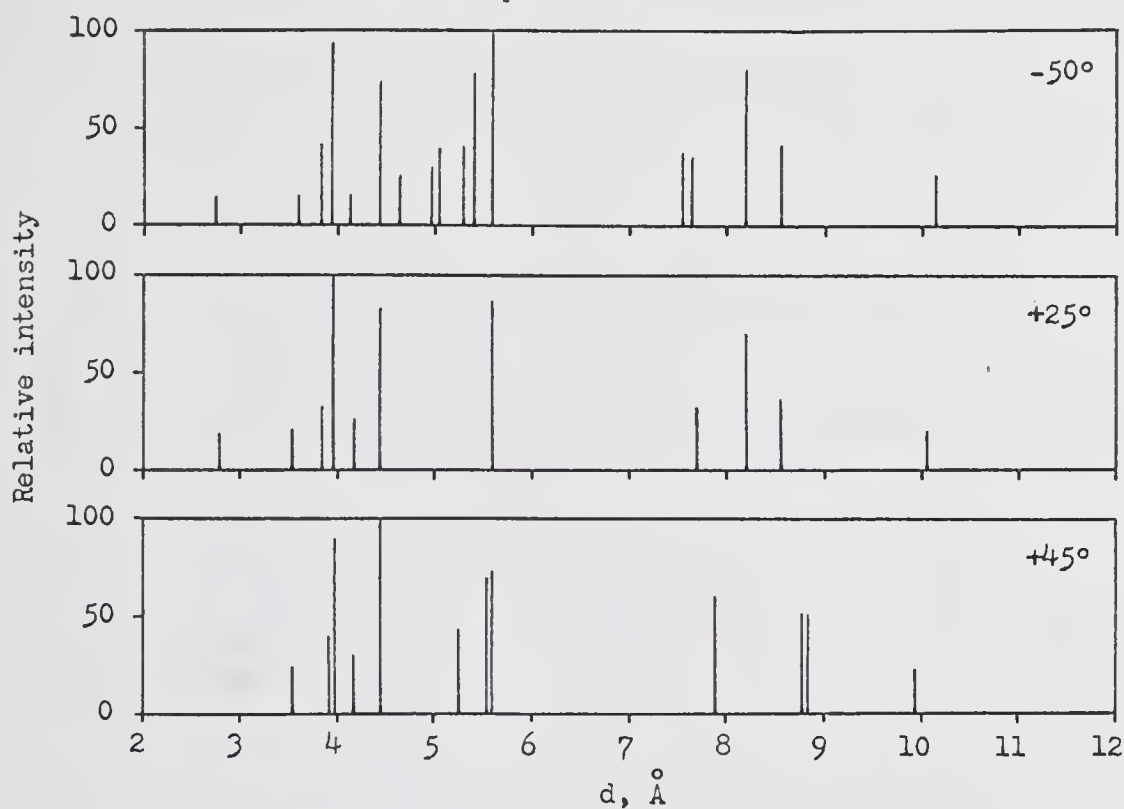


Fig. 43.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$  at three temperatures

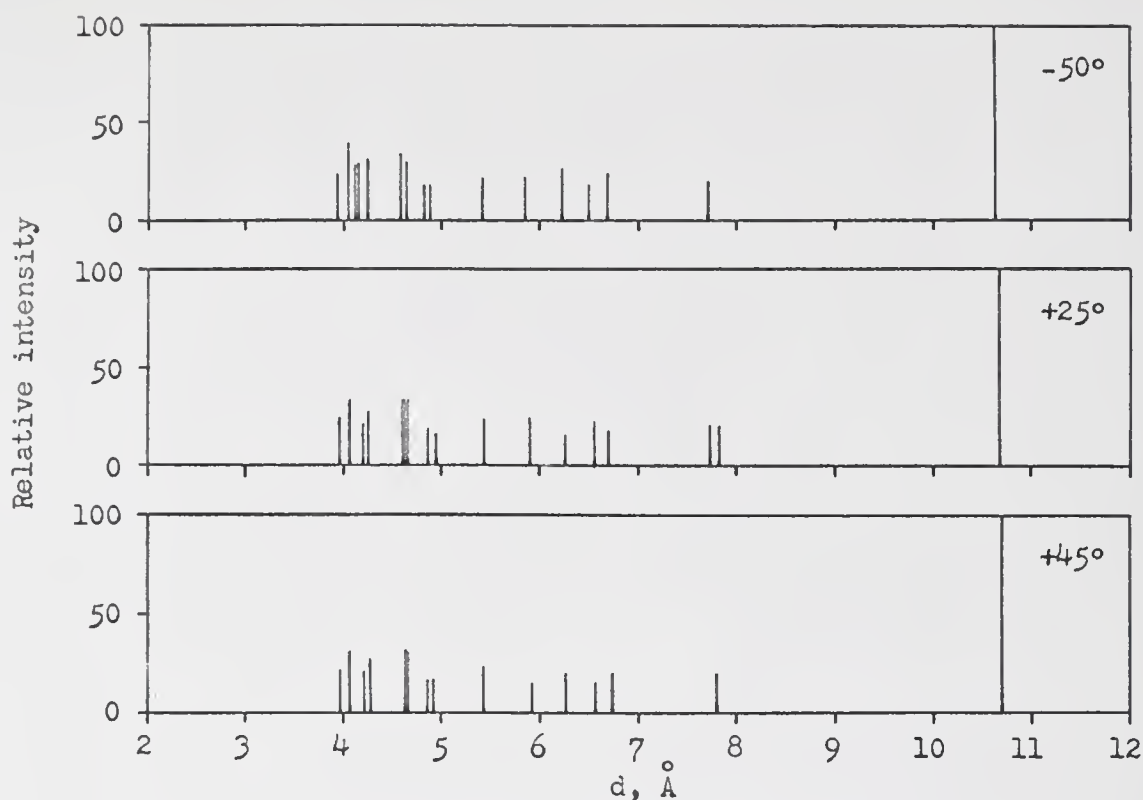


Fig. 44.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$  at three temperatures

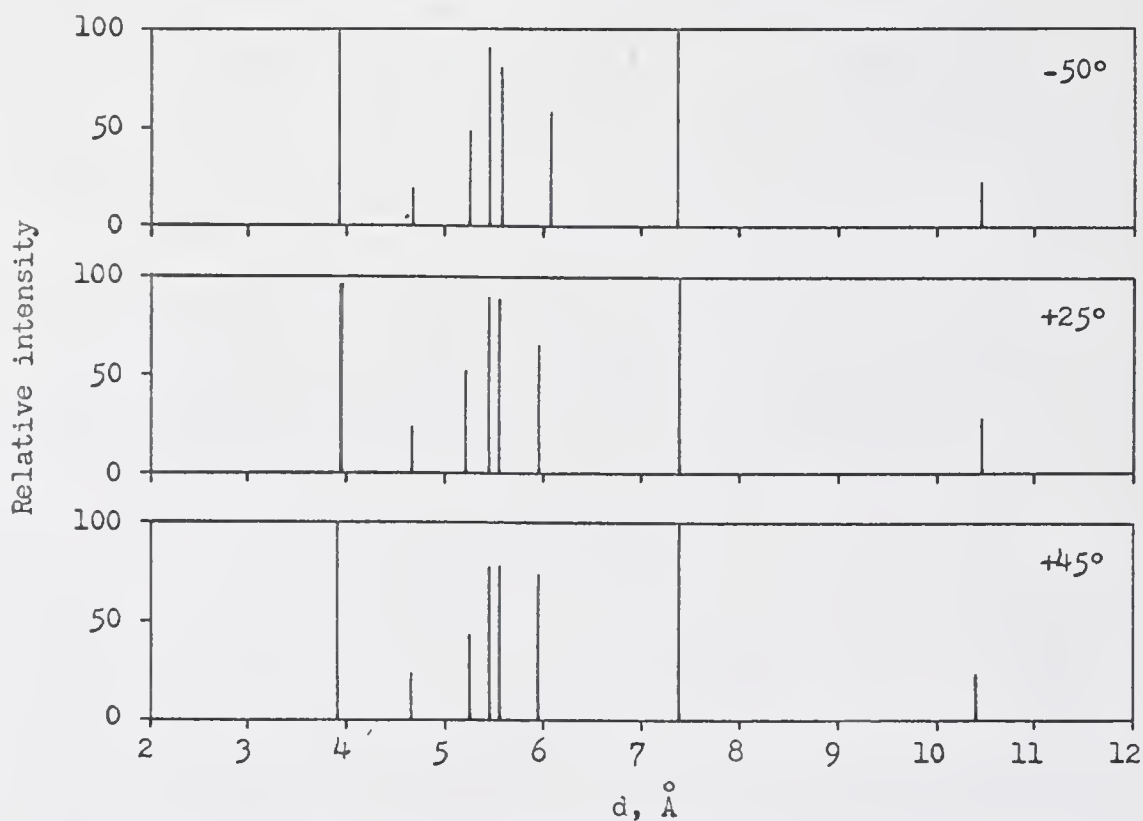


Fig. 45.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$  at three temperatures

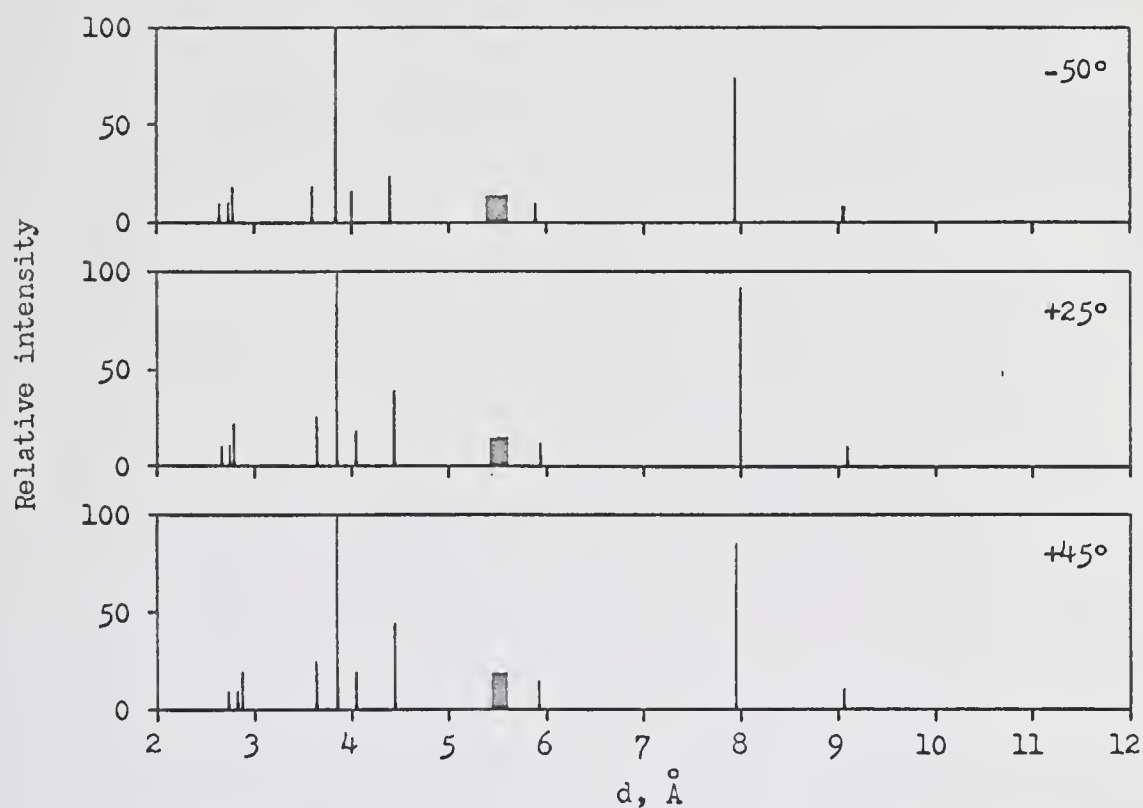


Fig. 46.- X-ray diffraction pattern of  $[\text{Co}(\text{terpy})_2](\text{NO}_3)_2$  at three temperatures



intensity is given a relative intensity of 100, upon which value all other relative intensities are based. Relative intensities less than 10 are generally omitted for reasons of clarity. Since most structural calculations are based on data other than d-spacings, a computer program was written with the aid of David L. Williams to calculate values of the angle theta, sine theta,  $\sin^2$  theta, and the d-spacings from the diffractometer measured value of two theta. The data are presented in Appendix II.

The three temperatures at which the diffraction measurements were made,  $-50^\circ$ ,  $+25^\circ$ , and  $+45^\circ\text{C}$ , gave a wide temperature range over which to observe possible changes of the gross crystal structure.  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  and  $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  undergo changes in their patterns as the compounds are heated from room temperature to  $45^\circ$ . Although their patterns differ at room temperature, they become identical at  $45^\circ$ . The most plausible explanation for the crystal change is that some water of hydration is being lost from each of the solids, with the result that both compounds possess the same structure and the same number of water molecules of hydration, if any, at  $+45^\circ$ . Pronounced structure changes are not apparent in any of the other complexes prepared during the course of this investigation.

It was hoped that from the X-ray diffraction data the complexes could be indexed according to crystal system, thus

enabling calculation of lattice parameters. Correlation of changes of the lattice parameters as a function of temperature with the magnetic behavior of the solid could perhaps yield valuable information concerning distortions as a function of temperature. Unfortunately, indexing was not successfully accomplished on the compounds because of the low symmetry typical of many coordination compounds (1,19).

#### Conductance Measurements

The equivalent conductance of several complexes was determined in dimethyl sulfoxide to detect the possible formation of ion pairs as experimentally observed in dimethyl formamide. Concentrations of 0.020 molar were used. The values observed were 27.5, 28.5, and 23.6  $\text{cm}^2 \text{equiv}^{-1} \text{ohm}^{-1}$  for  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$ ,  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$ , and  $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ . In addition, the conductance of a typical complex,  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$ , was measured over a tenfold range of concentrations. The linearity of the plot of equivalent conductance versus the square root of the equivalent concentration indicates that the existence of ion pairs in dimethyl sulfoxide is not an important factor in the concentrations used in this investigation (5).

## Spectral Measurements

Diffuse reflectance spectra of the complexes were measured and the positions of the peaks and shoulders are compiled in Table 13. Quantitative determinations of absorptivities are not possible with diffuse reflectance measurements and therefore are not reported.

Unfortunately, cobalt(II) complexes incorporating  $\alpha$ -diimine coordinating groups seldom give informative resolved spectra and therefore few interpretations have been reported. An energy level diagram (Figure 47) for the  $d^7$  ion in an octahedral field reveals that the three spin-allowed transitions are from the  ${}^4T_1({}^4F)$  ground state to the excited states  ${}^4T_2$ ,  ${}^4A_2$ , and  ${}^4T_1({}^4P)$ . The corresponding energies are  $0.8 \Delta$ ,  $1.8 \Delta$ , and  $0.6 \Delta + 15,400 \text{ cm}^{-1}$ , respectively (38). It is difficult to assign electronic transitions in the complexes prepared in this investigation according to this scheme. For example, if the lowest energy absorption of  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes ( $15,000 \text{ cm}^{-1}$ ) is assigned the  ${}^4T_1 \rightarrow {}^4T_2$  transition, the calculated value for  $\Delta$  would be  $18,600 \text{ cm}^{-1}$ . On the other hand, if the lowest energy absorption is assigned the  ${}^4T_1 \rightarrow {}^4A_2$  transition, the calculated value of  $\Delta$  would be  $8,300 \text{ cm}^{-1}$ . Since the expected value of  $\Delta$  is in the vicinity of  $14,000 \text{ cm}^{-1}$  (28,55), the two assignments normally possible are either unrealistically large or small. Nevertheless, the solution spectrum of  $[\text{Co}(\text{terpy})_2]^{2+}$

TABLE 13

DIFFUSE REFLECTANCE SPECTRA AND ELECTRON PARAMAGNETIC  
RESONANCE g VALUES

Complex	Wavelength, Å°	Wave- number cm <sup>-1</sup>	g Value
[Co(PvdH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	9,200 sh	10,880	2.14
	4,000	25,000	
[Co(PvdH) <sub>3</sub> ]Br <sub>2</sub>	9,000	11,000	2.13 <sup>a</sup>
	4,050	24,690	
[Co(PvdH) <sub>3</sub> ]I <sub>2</sub>	6,000 sh	16,650	2.14
	3,400 sh	29,400	
[Co(PvdH) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	3,900	25,600	2.13
	3,500	28,550	
[Co(PvdH) <sub>3</sub> ][B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	9,200 sh	10,880	2.08 <sup>b</sup>
	4,000	25,000	
[Co(BdH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	3,900	25,600	2.13
[Co(BdH) <sub>3</sub> ]Br <sub>2</sub>	8,750	11,450	2.13
	4,000	25,000	
[Co(BdH) <sub>3</sub> ]I <sub>2</sub>	12,000 sh	8,330	2.11 <sup>a</sup>
	9,200 sh	10,880	
	6,200 sh	16,130	
	5,150	19,430	
	4,000	25,000	
[Co(BdH) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	3,500 sh	28,550	2.09
[Co(BdH) <sub>3</sub> ][B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	3,500	28,550	2.09 <sup>b</sup>
	4,000	25,000	

Table 13 (cont'd)

Complex	Wavelength, Å°	Wave- number cm <sup>-1</sup>	g Value
[Co(terpy) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	6,700	14,920	2.11
	5,550	18,000	
	5,050	19,800	
	4,000	25,000	
[Co(terpy) <sub>2</sub> ]Cl <sub>2</sub> ·4H <sub>2</sub> O	6,700	14,920	2.08
	5,550	18,000	
	5,050	19,800	
	4,500	22,200	
[Co(terpy) <sub>2</sub> ]Cl <sub>2</sub> ·5H <sub>2</sub> O	6,700	14,920	2.09 <sup>a</sup>
	5,500	18,180	
	4,700	21,300	
[Co(terpy) <sub>2</sub> ]Br <sub>2</sub> ·H <sub>2</sub> O	6,700	14,920	2.08 <sup>a</sup>
	5,550	18,000	
	5,150	19,400	
	4,500	22,200	
[Co(terpy) <sub>2</sub> ]I <sub>2</sub> ·H <sub>2</sub> O	6,700	14,920	2.06
	5,600	17,850	
	5,100	19,600	
	3,700	27,000	
[Co(terpy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6,700	14,920	2.11
	5,550	18,000	
	5,100	19,600	
	3,600	27,800	
[Co(terpy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	5,500	18,200	2.06
	5,100	19,600	
	3,600	27,800	

Table 13 (cont'd)

Complex	Wavelength, Å°	Wave- number cm <sup>-1</sup>	g Value
[Co(terpy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O (anoxic)			2.09
[Co(terpy) <sub>2</sub> ]SO <sub>4</sub> ·2H <sub>2</sub> O	7,200	13,900	2.06
	5,600	17,850	
	5,100	19,600	
	4,500	22,200	
	3,550	28,200	
[Co(terpy) <sub>2</sub> ][B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	6,800	14,700	2.11 <sup>b</sup>
	5,550	18,000	
	5,100	19,600	
	4,500	22,200	
	3,250	30,800	

<sup>a</sup>Reference 50.<sup>b</sup>Averaged over hyperfine splitting.

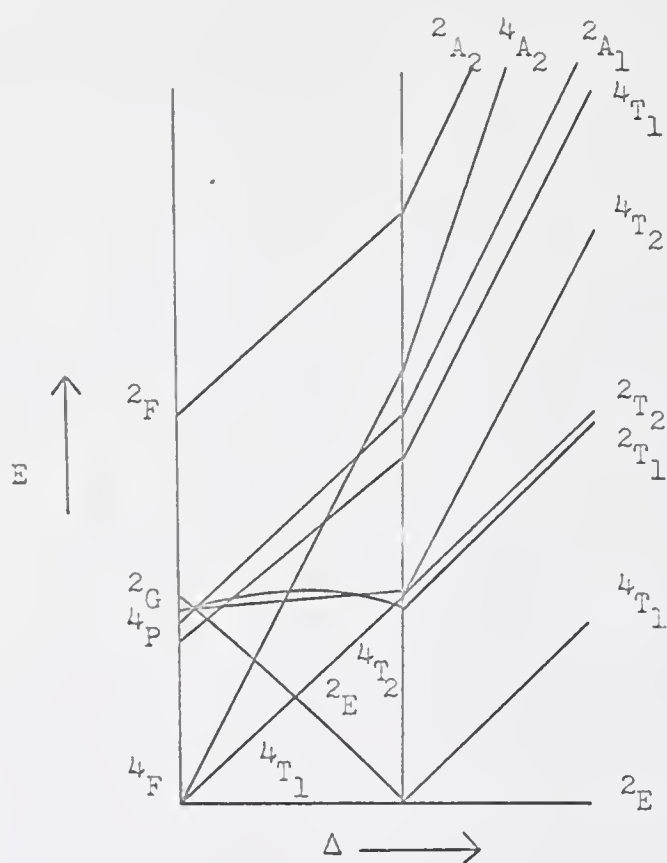


Fig. 47.- Energy level diagram for the  $d^7$  configuration in an octahedral field



indicate that the lowest energy absorption must be a d-d transition because of its broadness and absorptivity index (about 80). Similar difficulties are encountered in attempting to assign the absorptions of  $[\text{Co}(\text{PvdH})_3]^{2+}$  and  $[\text{Co}(\text{BdH})_3]^{2+}$  complexes.

The differences of the magnetic susceptibilities of  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes indicate that the cobalt(II) ion experiences a wide range of ligand field strengths contingent upon the anion in the crystal. This variation in the ligand field strength should be reflected in the electronic spectra (d-d transitions) of the complexes since both the magnetic moment and the spectra result from the electronic structure of the complex. The fact that the spectra observed for the  $[\text{Co}(\text{terpy})_2]^{2+}$  complexes are almost identical suggests that the absorptions are due to charge transfer transitions which are, to a first approximation, independent of the ligand field strength. On the other hand, the room-temperature magnetic moments of the complexes of the other two series are more nearly the same; therefore, the d-d transitions should occur at approximately the same positions. The positions of the absorptions of lowest energy typical of d-d transitions are not the same and consequently assignment of these absorptions is tenuous.

Each complex reported herein displays an electron paramagnetic resonance spectrum which is characteristic of



low-spin cobalt(II). The  $g$  values were calculated and are presented in Table 13. All values lie in the vicinity of  $2.10 \pm 0.04$ , within the range reported by Schmidt (50). It is concluded that every compound reported in this investigation, even  $[\text{Co}(\text{PvdH})_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$  which exhibits normal Curie-Weiss behavior, has a significant amount of low-spin species present at liquid nitrogen temperatures. Thus, in agreement with Schmidt (50), anomalous Curie-Weiss behavior is not a requisite for the existence of a Boltzmann distribution over spin states.

## DISCUSSION

Theoretically, there has been little reason to believe that a non-coordinated anion should have a significant effect upon the magnetic behavior of a coordination compound. In general, the crystal field spectra of inorganic complexes are independent (to within approximately 2 per cent) of the effect of anything outside the primary coordination sphere (38). Since both spectra and magnetic characteristics are intimately related to the electronic structure of the complex, the magnetic moment should be similarly independent of the effect of chemical species outside the primary coordination sphere. It is significant, therefore, that the anion of each complex prepared during the course of this investigation has a marked effect upon the magnetic susceptibility.

Dissolving the complexes in dimethyl sulfoxide or water removed the effects of the crystalline lattice. The solution magnetic moments observed were  $4.77 \pm 0.10$  B.M. for the  $[\text{Co}(\text{PvdH})_3]^{2+}$  series,  $4.60 \pm 0.10$  B.M. for the  $[\text{Co}(\text{BdH})_3]^{2+}$  series, and  $3.35 \pm 0.15$  B.M. for the  $[\text{Co}(\text{terpy})_2]^{2+}$  series. These moments indicate that the order of increasing ligand strength for these three ligands with cobalt(II) is  $\text{PvdH} \leq$

BdH < terpy. This order is reversed from the order with nickel(II):  $\text{terpy} \leq \text{BdH} < \text{PvdH}$ , indicative of differences of pi-bonding characteristics of the metal (38).

A few  $1/\chi$  versus  $T$  curves have been reported previously for anomalous cobalt(II) complexes (27,28,44,53,54,55). But the variety of curves has been increased considerably by the work done in the present study (Figures 1 through 23). Of the twenty complexes investigated, thirteen are reported for the first time, and seventeen are shown, for the first time, to exhibit anomalous Curie-Weiss behavior.

There are several possible explanations for the unusual effect of the anion. Considering the  $[\text{Co}(\text{PvdH})_3]^{2+}$  series, it is seen that the order of decreasing contribution of the anion to the low-spin character of the complex is  $\text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^- \geq \text{B}(\text{C}_6\text{H}_5)_4^-$ . It is immediately apparent that this is also the order of increasing anion size. The questionable ordering of  $\text{NO}_3^-$  with respect to size is reasonable if the planar  $\text{D}_{3h}$  symmetry of the ion is recalled. Whereas the other ions may be roughly considered to be spherical ions, that is, little change in apparent size by changing orientation, the effective size of the nitrate ion along the  $\text{D}_3$  axis is less than that along one of the  $\text{C}_2$  axes and is, in fact, less than the size of the other ions. Thus, the variation of the magnetic suscepti-

bilities of the salts of  $[\text{Co}(\text{PvdH})_3]^{2+}$  is correlated with the size of the anion.

The order listed above follows, incidentally, the order of the spectrochemical series (38). It must be pointed out, however, that the spectrochemical series applies to coordinated groups only. In all probability the anions of the compounds reported herein are not coordinated. Indeed, all available data indicate that pyruvaldihydrazone and biacetyldihydrazone act as bidentate ligands (28,45) and that terpyridine acts as a tridentate ligand (34,45). For example, infrared spectra provide convincing evidence that the anions are not within the coordination sphere. Non-coordinated nitrate and perchlorate ions customarily exhibit strong absorptions between 1300 and 1400  $\text{cm}^{-1}$  and between 1050 and 1170  $\text{cm}^{-1}$ , respectively (18,33). Upon coordination, however, the strong band of the nitrate ion is split into two new bands, one lying at 1480-1530  $\text{cm}^{-1}$  and the other at 1250-1290  $\text{cm}^{-1}$ ; the perchlorate band is similarly split into two bands occurring at approximately 1200 and 1000  $\text{cm}^{-1}$  (18,33). Splitting characteristic of coordinated anions such as this is not observed in the nitrate and perchlorate complexes prepared in this investigation.  $[\text{Co}(\text{PvdH})_3](\text{NO}_3)_2$  and  $[\text{Co}(\text{terpy})_2]\text{NO}_3)_2$  have bands which are only slightly split, absorbing at 1372 and 1332  $\text{cm}^{-1}$ , and 1341 and 1368  $\text{cm}^{-1}$ , respectively. The nitrate band of

$[\text{Co}(\text{BdH})_3](\text{NO}_3)_2$  is unsplit, appearing at  $1370 \text{ cm}^{-1}$ . All the perchlorate salts prepared herein exhibit single broad absorptions at approximately  $1085 \text{ cm}^{-1}$ . Thus, the infrared data of the nitrate and perchlorate salts indicate distinct non-coordinated ions by virtue of the positions of their absorption maxima. Similar data are unobtainable for the halide salts. But since the nitrate and perchlorate anions represent the extremes of the anomalous magnetic behavior, it is improbable that the halide salts, exhibiting intermediate anomalous magnetic behavior, would lie within the coordination sphere. Furthermore, if terpyridine were acting as a bidentate rather than a tridentate ligand, this would be evidenced in its infrared spectrum by a doubling of its ring vibrations; such doubling was not observed. Similar arguments obtain for the dihydrazone complexes.

The  $[\text{Co}(\text{BdH})_3]^{2+}$  system is similar to the  $[\text{Co}(\text{PvdH})_3]^{2+}$  system in several ways. Again a pronounced dependence of the susceptibility upon the anion is noted. Excluding, for the moment, the discussion of  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$  at temperatures below  $175^\circ\text{K}$ , it is observed that the anion order of decreasing contribution to the low-spin character of the complex is now  $\text{NO}_3^- > \text{B}(\text{C}_6\text{H}_5)_4^- > \text{I}^- > \text{Br}^- \geq \text{ClO}_4^-$ . This order cannot be directly correlated with the size of the anion as was done for the PvdH series. However, a rationalization for this difference can be found from a detailed



examination of the X-ray diffraction patterns of these complexes. Whereas the diffraction data of  $[\text{Co}(\text{PvdH})_3]\text{Br}_2$  and  $[\text{Co}(\text{PvdH})_3]\text{I}_2$  have similar line positions, indicating that these compounds are isomorphous, the complexes  $[\text{Co}(\text{BdH})_3]\text{Br}_2$  and  $[\text{Co}(\text{BdH})_3]\text{I}_2$  are distinctly not isomorphous since the bromide salt has considerably more lines than the iodide salt, denoting lower symmetry for this crystal system. Thus, it is probable that the reversal of the bromide and iodide order relative to  $[\text{Co}(\text{BdH})_3]^{2+}$  arises from the change in the crystal system. A similar circumstance exists with the tetraphenylboron salts.

Another exception to the size correlation is found in the magnetic behavior of  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$ . Above  $175^\circ\text{K}$  the complex behaves as expected, with the perchlorate anion producing a small contribution to the low-spin character of the complex; but, below  $175^\circ$  the magnetic moment drops sharply from 4.42 B.M. at  $175^\circ$  to 2.68 B.M. at  $135^\circ$ . As evidenced by the crystal structure and magnetic characteristics of  $[\text{Co}(\text{BdH})_3]\text{I}_2$  and  $[\text{Co}(\text{BdH})_3]\text{Br}_2$ , it appears that the crystal habit of the complex salt has an appreciable influence upon its degree of low-spin character. According to these observations, the unusual change in the  $1/\chi$  versus  $T$  curve of  $[\text{Co}(\text{BdH})_3](\text{ClO}_4)_2$  can be accounted for by a change in the crystal habit of the complex from one of large low-spin contribution to one of large high-spin contribution.

In order to fully substantiate this argument, it would be necessary to measure the X-ray diffraction pattern before and after the apparent change of phase. Unfortunately, the low temperatures required for such measurement could not be obtained by using the diffraction equipment available. Similar observations concerning unusual magnetic behavior resulting from an apparent change of phase have been reported by Ewald et al. (21).

The data for the complexes containing terpyridine are not quite so readily explained. The ordering of the anions with respect to the degree of contribution to low-spin character is more complicated in that there is a dependence of the order upon the temperature. In addition to the simple anion effect, there are effects arising from the number of water molecules of hydration and adsorbed oxygen.

At room temperature the order of contribution of the anion to the low-spin species is  $\text{Cl}^-(4\text{H}_2\text{O}) > \text{Cl}^-(5\text{H}_2\text{O}) > \text{Br}^-(\text{H}_2\text{O}) > \text{NO}_3^- \geq \text{SO}_4^{2-}(2\text{H}_2\text{O}) > \text{I}^-(\text{H}_2\text{O}) > \text{B}(\text{C}_6\text{H}_5)_4^-$  (excluding the perchlorate systems). Magnetic measurements made at intermediate temperatures gave a rather different order:  $\text{NO}_3^- \geq \text{Cl}^-(4\text{H}_2\text{O}) \geq \text{Br}^-(\text{H}_2\text{O}) > \text{Cl}^-(5\text{H}_2\text{O}) > \text{I}^-(\text{H}_2\text{O}) > \text{SO}_4^{2-}(2\text{H}_2\text{O}) > \text{B}(\text{C}_6\text{H}_5)_4^-$ . The lowest temperatures at which the measurements were made gave a still different order:  $\text{Br}^-(\text{H}_2\text{O}) \geq \text{NO}_3^- > \text{Cl}^-(4\text{H}_2\text{O}) > \text{Cl}^-(5\text{H}_2\text{O}) > \text{I}^-(\text{H}_2\text{O}) >$

$\text{SO}_4^{2-}(2\text{H}_2\text{O}) > \text{B}(\text{C}_6\text{H}_5)_4^-$ . Thus, at no temperature can it be said that the order strictly is the same as that observed with the  $[\text{Co}(\text{PvdH})_3]^{2+}$  or  $[\text{Co}(\text{BdH})_3]^{2+}$  systems.

Several items here deserve further attention. It has been shown in a concurrent investigation that anomalous  $1/\chi$  versus  $T$  curves can be theoretically duplicated by allowing the ligand field strength to be a function of temperature (56). The observations concerning the relative contributions of the nitrate and the bromide monohydrate with respect to the degree of low-spin character of the complex indicate that the change in the ligand field strength over the temperature range studied is not the same in each case. It is apparent from Figure 22 that the ligand field strength of the nitrate complex is changing at a more rapid rate than is that of the bromide monohydrate complex. Furthermore, since the curves are so nearly identical over a temperature range of approximately  $100^\circ$ , the sudden change of the nitrate indicates that the change in the ligand field strength with temperature is not uniform; rather, it is variable. Ostensibly, both the amount of change in the ligand field strength and its rate of change are very sensitive to the crystal system and other undetermined solid state effects.

The three  $[\text{Co}(\text{terpy})_2]^{2+}$  perchlorate complexes are quite illustrative of the extreme sensitivity of the magnetic



behavior of anomalous cobalt(II) complexes to solid state effects. Anhydrous  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$  was prepared essentially in the absence of water (cobalt(II) perchlorate hexahydrate was used as a starting material).

$[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  was prepared in a manner described by Hogg and Wilkins (34), that is, by the addition of an aqueous solution of sodium perchlorate to an aqueous solution containing the  $[\text{Co}(\text{terpy})_2]^{2+}$  ion. After drying the monohydrate product in vacuo, it was noticed that the compound became lighter in color upon exposure to air. This phenomenon could be reversed by again decreasing the atmospheric pressure over the complex. Although this compound has been synthesized and investigated by others (34,39,55), the particular observation made here has not been reported previously. Subsequent experiments disclosed that the color change occurred upon exposure to pure oxygen but not upon exposure to pure nitrogen, both obtained from commercial cylinders. This led to the conclusion that the compound adsorbs oxygen reversibly. For purposes of clarity, the oxygen-sensitive compound without oxygen is referred to as anoxic.

The magnetic behavior of  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  exposed to air does not differ greatly from that reported previously (55). Below 225°K normal Curie-Weiss behavior is followed with a large Weiss constant of 71°. From room

temperature to  $330^{\circ}$ , in which interval the  $1/\chi$  versus  $T$  curve is again linear, the Weiss constant is  $2^{\circ}$ . Previously reported data do not indicate the break in the curve which is reported here; however, the data included herein are reproducible.

The anoxic compound behaves magnetically very differently from the one exposed to air. A pronounced maximum in the  $1/\chi$  versus  $T$  plot is obtained, and at low temperatures the magnetic moment drops to 1.96 B.M. The anhydrous compound exhibits magnetic behavior intermediate between the other two perchlorates. From the X-ray diffraction patterns it is obvious that the anhydrous and the hydrated perchlorates are not isomorphous. (The diffraction pattern of the anoxic compound was not obtained because of experimental difficulties.) The fact that the salts are not isomorphous again suggests that one crystal system allows room for the water of hydration and/or oxygen whereas the other does not, and that the magnetic behavior is dependent upon the crystal system of the complex salt.

Infrared spectral measurements made on a Nujol mull of the anoxic compound showed no absorptions between 3100 and  $4000\text{ cm}^{-1}$ . After exposing the compound to air, absorptions appeared at 3530 and  $3600\text{ cm}^{-1}$ . This is in the region of O-H symmetric and asymmetric stretching vibrations. From these data alone it appears that the anoxic compound might

actually be another crystalline form of anhydrous  $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$ , adsorbing moisture reversibly upon exposure to air and oxygen. It is difficult to believe, however, that commercial oxygen in high-pressure cylinders contains sufficient moisture to cause the pronounced color change that was observed. Further investigation of a more refined nature needs to be carried out on the adsorption properties of this compound.

Having established a rough correlation between anion size and magnetic properties of complexes, it is tempting to speculate about some of the factors responsible for the correlation. The complex cations in these compounds are very large ions relative to the anions, the disparity being largest (greatest mismatch of size) for the  $\text{Cl}^-$  or  $\text{NO}_3^-$  salts and smallest for the  $\text{B}(\text{C}_6\text{H}_5)_4^-$  salts. Very approximate sizes and radius ratios are given in Table 14 (43). A possible consequence of extreme mismatch of size is cation-anion contact and a concomitantly small lattice energy. Thus, the larger the size of the anion, the more stable the lattice. Some support for this conclusion is found in the qualitative observation that solubility of complex salts of this kind decreases as anion size increases. Additional lattice stabilization could be gained by decreasing the size of the complex cation, a realizable phenomenon for complex cations which can exist in two different spin states because

TABLE 14  
APPROXIMATE SIZES OF IONS

Ion	Diameter, Å°	<u>Anion radius</u> <u>cation radius</u>
$[\text{Co}(\text{terpy})_2]^{2+}$	11.74	-
$\text{B}(\text{C}_6\text{H}_5)_4^-$	8.92	0.76
$\text{SO}_4^{=}$	5.04	0.43
$\text{ClO}_4^-$	4.98	0.42
$\text{I}^-$	4.43	0.38
$\text{Br}^-$	3.80	0.32
$\text{Cl}^-$	3.60	0.31
$\text{NO}_3^-$	1.48	0.13

the ionic volume of the low-spin form is less than that of the high-spin form (21,37). Ewald et al. have demonstrated that a relatively small change of ionic volume produces significant changes in the magnetic moments of ions in the vicinity of the cross-over point (21).

The above conclusions are entirely consistent with past knowledge concerning packing in crystals. The way in which all ions, complex or simple, pack together in a crystal is determined by geometrical considerations, that is, by their relative sizes and by the relative numbers of the different kinds of ions. Thus, it is to be expected that varying the anion or the number of water molecules of hydration will cause different crystal packing. Consequently, the complex cation will experience different distortions from approximately octahedral symmetry and different electronic influences from the remaining members of the crystal. In the region near the cross-over point it is reasonable that the magnetic behavior might be very sensitive to rather small changes in symmetry and environment. Even though quantitative measurements of crystalline parameters were not made, it has been demonstrated dramatically that solid state effects are of major importance in determining the magnetic behavior of cobalt(II) complexes near the cross-over point.

## SUMMARY

Twenty cobalt(II) complexes of pyruvaldihydrazone, biacetyldihydrazone, and terpyridine were considered during the course of this investigation, thirteen of which have not been reported previously. These complexes were characterized by their magnetic behavior, both in crystalline form and in solution, and by X-ray diffraction patterns, electron paramagnetic resonance spectra, and electronic spectra. The X-ray diffraction patterns and the magnetic behavior of the solids were determined as a function of temperature.

The room-temperature magnetic moments of the complexes are intermediate between the values customarily exhibited by normal high- and low-spin octahedral cobalt(II) species. Nineteen of the complexes are shown, for the first time, to exhibit anomalous Curie-Weiss behavior. Electron paramagnetic resonance data provide convincing evidence of the presence of the low-spin cobalt(II) species in each complex. X-ray diffraction data preclude the possibility in all but one instance that gross structural changes are responsible for the anomalous Curie-Weiss behavior.

It was demonstrated that the magnetic behavior of salts of cobalt(II) complexes in the vicinity of the cross-



over point depends markedly upon solid state effects introduced by variations of anion size, the number of water molecules of hydration, and the crystal system of the complex. To further demonstrate the solid state effects, the complexes were dissolved in dimethyl sulfoxide or water and the magnetic moments measured; the solution magnetic moments thus obtained were the same for all the salts of a given complex cation. Using solution moments as a criterion for the relative ligand field strengths of the ligands, the order of increasing effective basicity for these ligands is pyruvaldihydrazone  $\leq$  biacetyldihydrazone  $<$  terpyridine.

## APPENDICES



## APPENDIX I

The magnetic susceptibilities of the complexes were corrected for diamagnetism of the ligands by using Pascal's constants and of the anions and metal ion by using experimentally determined values (52).

TABLE 15

## SUSCEPTIBILITY CORRECTIONS FOR DIAMAGNETISM

C	- $6.00 \times 10^{-6}$ c.g.s. units
H	- 2.93
N	- 5.55
O	- 4.61
Cl <sup>-</sup>	-20.1
Br <sup>-</sup>	-30.6
I <sup>-</sup>	-52.00
Co(II)	-12.0
B	- 0.2
ClO <sub>4</sub> <sup>-</sup>	-34.0
NO <sub>3</sub> <sup>-</sup>	-20.0
C=N-	+ 8.15
C <sub>6</sub> H <sub>5</sub>	- 1.4
SO <sub>4</sub> <sup>=</sup>	-40.0

## APPENDIX II

TABLE 16

## COMPLETE X-RAY DIFFRACTION PATTERNS OF COMPLEXES

2 $\theta$	Sin $\theta$	Sin <sup>2</sup> $\theta$	D	Relative Intensity
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## Tris(Pyruvaldihydrazone)Cobalt(II) Bromide

Temperature = -50°

11.54	.10054	.01011	7.669	49
16.34	.14211	.02020	5.425	40
16.82	.14626	.02139	5.272	100
20.12	.17468	.03051	4.414	87
21.03	.18249	.03330	4.225	25
23.57	.20424	.04171	3.775	37
26.31-	.22759	.05180	3.388	51
26.37	.22810	.05203	3.380	53
30.91	.26648	.07101	2.893	13
31.93	.27505	.07565	2.803	16
33.35	.28694	.08234	2.687	20
35.25	.30279	.09168	2.546	15

Temperature = +25°

11.50	.10019	.01004	7.696	46
16.37	.14237	.02027	5.415	35
16.80	.14608	.02134	5.278	100
20.02	.17332	.03021	4.436	84
20.95	.18131	.03305	4.241	26
23.51	.20373	.04150	3.784	36
26.30	.22750	.05176	3.389	52
30.83	.26581	.07065	2.901	12
31.88	.27463	.07542	2.807	17
33.30	.28652	.08210	2.691	26
35.12	.30170	.09103	2.555	18

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
Temperature = +45°				
11.48	.10001	.01000	7.709	46
15.93	.13857	.01920	5.564	31
16.26	.14142	.02000	5.452	34
16.78	.14591	.02129	5.284	100
20.01	.17373	.03018	4.438	83
20.95	.18181	.03305	4.241	26
23.51	.20373	.04150	3.784	38
26.24 -	.22699	.05152	3.397	53
26.29	.22742	.05172	3.390	53
30.78 -	.26539	.07043	2.905	14
30.88	.26623	.07088	2.896	14
31.88	.27463	.07542	2.807	16
33.24 -	.28602	.08181	2.696	23
33.31	.28661	.08214	2.690	23
35.03	.30096	.09057	2.562	18

Tris(Pyruvaldihydrazone)Cobalt(II) Iodide

Temperature = -50°

16.02	.13935	.01942	5.533	34
16.66	.14487	.02099	5.322	72
19.90	.17279	.02986	4.462	100
20.77	.18026	.03249	4.277	12
23.34	.20227	.04091	3.812	48
26.10	.22580	.05099	3.415	61
26.90	.23260	.05410	3.315	17
30.65	.26429	.06985	2.917	16
33.10	.28485	.08114	2.707	15
34.91	.29996	.08997	2.570	17

Temperature = +25°

15.93	.13857	.01920	5.564	34
16.53	.14375	.02066	5.363	78
19.78	.17176	.02950	4.469	100
20.70	.17966	.03228	4.291	10
23.20	.20108	.04043	3.834	48
25.92	.22427	.05030	3.438	62
26.70 -	.23090	.05331	3.339	15
26.95	.23302	.05430	3.309	15
30.51	.26312	.06923	2.930	17
32.90	.28318	.08019	2.723	20
34.70	.29821	.08893	2.585	18

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
Temperature = $+45^\circ$				
16.01	.13926	.01939	5.536	40
16.57	.14410	.02076	5.351	82
19.83	.17219	.02965	4.478	100
20.73	.17992	.03237	4.285	12
23.25	.20151	.04060	3.826	47
25.97	.22470	.05049	3.431	66
26.80-	.23175	.05371	3.327	18
26.96	.23311	.05434	3.308	18
30.50	.26303	.06919	2.931	16
32.91	.28326	.08024	2.722	21
34.72	.29837	.08903	2.584	16

Tris(Pyruvaldihydrazone)Cobalt(II) Perchlorate

Temperature = $-50^\circ$				
11.20	.09758	.00952	7.901	14
15.89	.13822	.01911	5.578	100
19.55	.16978	.02883	4.541	35
20.37	.17683	.03127	4.360	16
22.62	.19612	.03846	3.931	20
25.35	.21942	.04815	3.514	61

Temperature = $+25^\circ$				
11.18	.09741	.00949	7.915	13
15.85	.13788	.01901	5.592	106
19.38	.16832	.02833	4.581	30
20.24	.17571	.03087	4.388	16
22.49	.19500	.03803	3.954	21
25.23	.21840	.04770	3.530	63

Temperature = $+45^\circ$				
11.19	.09750	.00951	7.908	14
15.88	.13814	.01908	5.581	100
19.38	.16832	.02833	4.581	32
20.20	.17557	.03075	4.397	14
22.50	.19509	.03806	3.952	17
25.22	.21831	.04766	3.532	62

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
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Tris(Pyruvaldihydrazone)Cobalt(II) Nitrate

Temperature =  $-50^\circ$

11.41	.09941	.00988	7.756	100
15.25	.13269	.01761	5.811	36
16.09	.13995	.01959	5.509	100
17.74	.15419	.02378	5.000	29
19.77	.17167	.02947	4.491	33
24.48	.21201	.04495	3.637	13
25.13	.21755	.04733	3.544	52

Temperature =  $+25^\circ$

11.32	.09862	.00973	7.817	89
15.25	.13269	.01761	5.811	38
16.09	.13995	.01959	5.509	100
17.55	.15255	.02327	5.054	27
19.71	.17116	.02929	4.505	29
24.92-	.21576	.04655	3.573	41
25.15	.21772	.04740	3.541	41
28.30	.24446	.05976	3.154	20

Temperature =  $+45^\circ$

11.32	.09862	.00973	7.817	86
15.20	.13226	.01749	5.830	37
16.09	.13995	.01959	5.509	100
17.56	.15264	.02330	5.051	26
19.74	.17141	.02938	4.498	35
24.93-	.21584	.04659	3.572	44
25.15	.21772	.04740	3.541	44
28.12	.24294	.05902	3.174	25

Tris(Pyruvaldihydrazone)Cobalt(II) Tetraphenyl Boron

Temperature =  $-50^\circ$

7.12	.06209	.00386	12.417	35
14.89	.12957	.01679	5.950	47
15.93-	.13857	.01920	5.564	100
16.42	.14280	.02039	5.399	100
19.78	.17176	.02950	4.489	40

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
20.44	.17743	.03148	4.345	42
21.57	.18712	.03502	4.120	17
23.18	.20091	.04036	3.838	19
25.03	.21670	.04696	3.558	28

Temperature = +25°

7.15	.06235	.00389	12.365	36
14.88	.12949	.01677	5.954	33
15.95-	.13874	.01925	5.557	100
16.35	.14220	.02022	5.422	100
19.79	.17184	.02953	4.487	37
20.30	.17623	.03106	4.375	37
21.58	.18721	.03505	4.118	20
23.15	.20065	.04026	3.843	16
24.90	.21559	.04648	3.576	30

Temperature = +45°

7.15	.06235	.00389	12.365	27
14.87	.12940	.01674	5.958	36
15.95	.13874	.01925	5.557	99
16.24	.14125	.01995	5.459	100
19.78	.17176	.02950	4.489	32
20.24	.17571	.03087	4.388	32
21.60	.18738	.03511	4.115	14
23.14	.20056	.04023	3.844	19
24.86	.21525	.04633	3.582	25

Tris(Biacetyldihydrazone)Cobalt(II) Bromide

Temperature = -50°

10.57	.09211	.00848	8.370	59
14.00	.12187	.01485	6.326	39
16.02	.13935	.01942	5.533	37
16.32	.14194	.02015	5.432	34
17.08	.14850	.02205	5.192	25
17.98	.15626	.02442	4.934	36
18.95	.16462	.02710	4.684	24
20.07	.17425	.03036	4.425	100
22.00	.19081	.03641	4.041	30
22.72	.19697	.03880	3.914	10
23.91	.20714	.04291	3.722	22

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
24.68	.21371	.04567	3.608	16
25.85	.22368	.05003	3.447	54
26.12	.22597	.05106	3.412	22
27.20	.23514	.05529	3.279	25
27.98	.24175	.05844	3.189	23
28.30	.24446	.05976	3.154	44
29.87	.25772	.06642	2.992	21
30.53	.26328	.06932	2.928	23
31.75	.27354	.07482	2.819	18
32.53	.28008	.07844	2.753	68
32.97	.28376	.08052	2.717	16
33.48	.28803	.08296	2.677	11
34.41	.29579	.08749	2.607	16
35.93	.30844	.09513	2.500	12
38.32	.32821	.10772	2.349	15
39.80	.34038	.11586	2.265	10

Temperature = +25°

10.50	.09150	.00837	8.426	57
13.96	.12152	.01477	6.344	45
15.87	.13805	.01906	5.585	39
15.94	.13865	.01923	5.561	38
16.25	.14133	.01998	5.455	33
17.14	.14902	.02221	5.174	22
17.82	.15488	.02399	4.978	36
17.88	.15540	.02415	4.961	43
18.87	.16393	.02687	4.703	23
19.96	.17330	.03003	4.449	100
21.86	.18961	.03595	4.066	23
22.62	.19612	.03846	3.931	10
23.74	.20569	.04231	3.748	19
24.67	.21363	.04564	3.609	15
25.73	.22265	.04957	3.463	49
27.02	.23361	.05458	3.300	24
27.80	.24023	.05771	3.209	26
28.20	.24361	.05935	3.165	41
29.65	.25587	.06547	3.013	26
30.38	.26202	.06865	2.943	17
31.67	.27287	.07446	2.826	19
32.37	.27874	.07770	2.766	58
32.90	.28318	.08019	2.723	16
33.25	.28611	.08186	2.695	9
34.25	.29446	.08670	2.618	14
35.70	.30653	.09396	2.515	11
38.17	.32697	.10691	2.358	15
39.65	.33915	.11502	2.273	10



$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
10.53	.09176	.00842	8.402	76
14.00	.12187	.01485	6.326	31
16.03	.13943	.01944	5.530	34
16.32	.14194	.02015	5.432	27
17.14	.14902	.02221	5.174	23
17.88	.15540	.02415	4.961	39
18.90	.16419	.02696	4.696	23
19.98	.17348	.03009	4.444	100
21.14	.18344	.03365	4.203	9
21.54	.18687	.03492	4.126	12
21.90	.18995	.03608	4.059	24
22.66	.19646	.03860	3.924	12
23.74	.20569	.04231	3.748	24
24.68	.21371	.04567	3.608	16
25.73	.22265	.04957	3.463	69
27.02	.23361	.05458	3.300	23
27.81	.24031	.05775	3.208	23
28.24	.24395	.05951	3.160	38
29.68	.25612	.06560	3.010	16
30.43	.26244	.06888	2.938	17
31.62-	.27245	.07423	2.830	17
31.75	.27354	.07482	2.819	17
32.36	.27866	.07765	2.767	68
32.98	.28385	.08057	2.716	16
33.51	.28828	.08311	2.674	12
34.10-	.29321	.08597	2.630	10
34.22	.29421	.08656	2.621	10
35.74	.30686	.09416	2.513	16

Tris(Biacetyldihydrazone)Cobalt(II) Iodide

Temperature =  $-50^\circ$  .

11.98	.10435	.01089	7.388	19
15.27	.13286	.01765	5.803	34
15.82	.13762	.01894	5.602	58
16.13	.14030	.01968	5.496	72
19.68	.17090	.02921	4.511	56
20.02	.17382	.03021	4.436	35
22.30	.19338	.03740	3.987	26
24.40	.21132	.04466	3.648	40
25.18	.21797	.04751	3.537	100
30.23	.26076	.06799	2.957	45
30.72	.26488	.07016	2.911	40
32.22	.27748	.07700	2.779	25



$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
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Temperature = +25°

11.95	.10409	.01084	7.407	22
15.30	.13312	.01772	5.792	43
15.79	.13736	.01887	5.613	66
16.10	.14004	.01961	5.506	77
19.63	.17047	.02906	4.523	59
19.90	.17279	.02986	4.462	28
22.28	.19321	.03733	3.991	26
24.34	.21081	.04444	3.657	39
25.14	.21763	.04736	3.543	100
30.08	.25949	.06734	2.971	47
30.50	.26303	.06919	2.931	43
32.08	.27631	.07635	2.790	19

Temperature = +45°

11.94	.10401	.01082	7.413	19
15.27	.13286	.01765	5.803	46
15.77	.13719	.01882	5.620	70
16.08	.13986	.01956	5.512	92
19.58	.17004	.02891	4.534	69
19.88	.17262	.02980	4.467	40
22.18	.19235	.03700	4.008	29
24.30	.21047	.04430	3.663	40
25.12	.21746	.04729	3.545	100
29.97	.25857	.06686	2.982	53
30.44	.26253	.06892	2.937	37
32.00	.27564	.07598	2.797	32

Tris(Biacetyldihydrazone)Cobalt(II) Perchlorate

Temperature = -50°

10.56	.09202	.00847	8.378	34
11.00	.09585	.00919	8.044	21
15.60-	.13572	.01842	5.681	66
15.68	.13641	.01861	5.652	66
16.25	.14133	.01998	5.455	25
16.36	.14228	.02024	5.419	23
18.43	.16014	.02564	4.815	30
19.18	.16660	.02775	4.628	16
19.35	.16806	.02824	4.588	11
19.43	.16875	.02848	4.569	20

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
24.28-	.21030	.04423	3.666	100
24.39	.21124	.04462	3.650	100
25.49	.22061	.04867	3.495	52
34.48	.29637	.08784	2.601	46

Temperature = +25°

10.49	.09141	.00836	8.434	16
15.58-	.13554	.01837	5.688	95
15.72	.13675	.01870	5.638	95
15.95	.13874	.01925	5.557	48
16.25	.14133	.01998	5.455	41
18.35	.15945	.02542	4.835	38
19.18-	.16660	.02775	4.628	21
19.25	.16720	.02796	4.611	21
24.20-	.20962	.04394	3.678	100
24.26	.21013	.04415	3.669	100
25.52-	.22087	.04878	3.491	29
25.66	.22206	.04931	3.472	29
34.68	.29804	.08883	2.587	25

Temperature = +45°

10.43	.09089	.00826	8.482	15
15.63	.13597	.01849	5.670	100
16.08	.13986	.01956	5.512	46
18.32	.15919	.02534	4.843	36
19.20	.16677	.02781	4.623	21
24.22	.20979	.04401	3.675	86
25.63	.22180	.04920	3.476	28
34.09-	.29312	.08592	2.630	17
34.24	.29437	.08666	2.619	17

### Tris(Biacetyldihydrazone)Cobalt(II) Nitrate

Temperature = -50°

10.66	.09289	.00863	8.300	53
10.83	.09437	.00891	8.170	57
11.48	.10001	.01000	7.709	40
11.78	.10262	.01053	7.513	20
14.35-	.12490	.01560	6.173	24
14.45	.12577	.01582	6.130	24
14.62-	.12724	.01619	6.060	36
14.75	.12836	.01648	6.006	36

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
15.48	.13468	.01814	5.725	54
15.75	.13701	.01877	5.627	49
16.22-	.14107	.01990	5.465	100
16.27	.14151	.02002	5.449	100
16.88	.14677	.02154	5.253	32
18.48	.16057	.02578	4.802	19
20.80-	.18052	.03259	4.271	15
20.90	.18138	.03290	4.251	15
21.65	.18781	.03527	4.105	10
22.58	.19577	.03833	3.938	11
24.08	.20859	.04351	3.696	17
24.52	.21235	.04509	3.631	11
26.70	.23090	.05331	3.339	9
27.42	.23701	.05617	3.253	15
29.52	.25477	.06491	3.026	13

Temperature = +25°

10.65-	.09280	.00861	8.308	60
10.78	.09393	.00882	8.208	60
11.08	.09654	.00932	7.986	26
11.37-	.09906	.00981	7.783	49
11.47	.09993	.00999	7.716	49
11.70-	.10192	.01039	7.564	28
11.85	.10323	.01066	7.469	28
14.35	.12490	.01560	6.173	40
14.60	.12706	.01615	6.068	33
15.63	.13597	.01849	5.670	63
16.10-	.14004	.01961	5.506	100
16.20	.14090	.01985	5.472	100
16.85	.14651	.02147	5.262	28
18.30	.15902	.02529	4.848	20
20.73	.17992	.03237	4.285	20
21.85	.18952	.03592	4.068	11
22.56	.19560	.03826	3.942	11
23.22	.20125	.04050	3.831	17
24.00	.20791	.04323	3.708	31
24.44	.21167	.04480	3.643	23
24.95	.21601	.04666	3.569	10
25.83	.22351	.04995	3.450	18
26.48	.22903	.05245	3.366	16
27.19-	.23506	.05525	3.280	17
27.30	.23599	.05569	3.267	17

2 $\theta$	Sin $\theta$	Sin <sup>2</sup> $\theta$	D	Relative Intensity
Temperature = +45°				
10.68	.09307	.00866	8.284	32
10.77	.09385	.00881	8.215	33
11.03	.09611	.00924	8.022	48
11.35-	.09889	.00978	7.797	29
11.45	.09975	.00995	7.729	29
11.82	.10297	.01060	7.488	34
14.35-	.12490	.01560	6.173	29
14.47	.12594	.01586	6.122	29
14.58-	.12689	.01610	6.076	36
14.68	.12776	.01632	6.035	36
15.60	.13572	.01842	5.681	84
15.65-	.13615	.01854	5.663	87
15.71	.13667	.01868	5.641	87
16.15-	.14047	.01973	5.489	100
16.28	.14159	.02005	5.445	100
16.85	.14651	.02147	5.262	29
18.32	.15919	.02534	4.843	17
19.52	.16952	.02874	4.548	20
20.67	.17940	.03219	4.298	17
20.79	.18043	.03256	4.273	19
21.85	.18952	.03592	4.068	18
22.69	.19672	.03870	3.919	16
23.18	.20091	.04036	3.838	17
23.98	.20774	.04316	3.711	20
24.48	.21201	.04495	3.637	21
24.95	.21601	.04666	3.569	16
25.92	.22427	.05030	3.438	16
26.42	.22852	.05222	3.374	19
29.32	.25308	.06405	3.046	24
30.23	.26076	.06799	2.957	21

Tris(Biacetyldihydrazone)Cobalt(II) Tetraphenyl Boron

Temperature = -50°

8.15	.07106	.00505	10.850	43
8.54	.07446	.00554	10.355	21
9.24	.08055	.00649	9.572	29
12.90	.11234	.01262	6.863	20
13.00	.11320	.01281	6.811	27
13.50	.11754	.01382	6.560	33
14.23	.12386	.01534	6.225	22

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
14.78	.12862	.01654	5.994	70
16.28	.14159	.02005	5.445	100
16.90	.14695	.02159	5.247	74
17.74	.15419	.02378	5.000	49
19.28	.16746	.02804	4.604	48
21.42	.18584	.03454	4.149	37
23.48	.20347	.04140	3.789	21
25.85	.22368	.05003	3.447	23
26.35	.22793	.05195	3.383	25

Temperature = +25°

8.15	.07106	.00505	10.850	36
8.58	.07480	.00560	10.307	26
9.25	.08063	.00650	9.562	26
12.85	.11190	.01252	6.890	22
13.03	.11346	.01287	6.795	28
13.53	.11780	.01388	6.545	27
14.24	.12395	.01536	6.220	23
14.84	.12914	.01668	5.970	53
16.28	.14159	.02005	5.445	100
16.91	.14703	.02162	5.244	44
17.74	.15419	.02378	5.000	44
19.35	.16806	.02824	4.588	36
21.41	.18575	.03450	4.151	34
23.37	.20253	.04102	3.807	16
25.75	.22282	.04965	3.460	19
26.30	.22750	.05176	3.389	21

Temperature = +45°

8.05-	.07019	.00493	10.984	34
8.20	.07150	.00511	10.784	34
8.50	.07411	.00549	10.404	27
9.20	.08020	.00643	9.614	32
12.89	.11225	.01260	6.869	24
12.97	.11294	.01276	6.826	24
13.42	.11684	.01365	6.599	25
14.18	.12343	.01523	6.247	19
14.70	.12793	.01637	6.027	53
16.20	.14090	.01985	5.472	100
16.75	.14565	.02121	5.293	52
16.83	.14634	.02142	5.268	50
17.68	.15368	.02362	5.017	44
19.27	.16737	.02801	4.607	48
21.35	.18524	.03431	4.162	30



$2\theta$	$\sin\theta$	$\sin^2\theta$	D	Relative Intensity
23.27	.20168	.04067	3.823	16
25.70	.22240	.04946	3.467	19
26.30	.22750	.05176	3.389	25

Bis(Terpyridine)Cobalt(II) Chloride Pentahydrate

Temperature =  $-50^\circ$

9.30	.08107	.00657	9.510	52
10.09	.08794	.00773	8.768	50
10.41	.09072	.00823	8.499	20
10.82	.09428	.00889	8.178	29
14.01	.12196	.01487	6.322	39
15.87-	.13805	.01906	5.585	46
16.27	.14151	.02002	5.449	46
18.69	.16238	.02637	4.748	22
22.33	.19363	.03749	3.982	66
22.62	.19612	.03846	3.931	100
23.61	.20458	.04185	3.769	100
32.37	.27874	.07770	2.766	29

Temperature =  $+25^\circ$

9.29	.08098	.00656	9.521	43
10.12	.08820	.00778	8.742	43
10.84	.09446	.00892	8.163	36
13.97	.12161	.01479	6.340	39
15.83-	.13770	.01896	5.599	58
16.30	.14177	.02010	5.439	58
18.45-	.16031	.02570	4.809	22
18.60	.16160	.02612	4.771	22
22.40	.19423	.03773	3.969	67
22.62	.19612	.03846	3.931	100
23.60	.20450	.04182	3.770	84
32.30	.27815	.07737	2.772	22

Temperature =  $+45^\circ$

10.05	.08759	.00767	8.802	48
11.16	.09724	.00945	7.929	83
15.75-	.13701	.01877	5.627	50
16.23	.14116	.01993	5.462	50
20.08	.17434	.03039	4.423	52
23.02	.19954	.03982	3.864	100
24.70	.21388	.04575	3.605	22
32.02	.27580	.07607	2.795	27

$2\theta$	$\sin\theta$	$\sin^2\theta$	D	Relative Intensity
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## Bis(Terpyridine)Cobalt(II) Chloride Tetrahydrate

Temperature =  $-50^\circ$ 

9.24	.08055	.00649	9.572	44
10.02	.08733	.00763	8.829	42
10.68-	.09307	.00866	8.284	21
10.80	.09411	.00886	8.193	21
15.95	.13874	.01925	5.557	57
16.40	.14263	.02034	5.406	57
18.60	.16160	.02612	4.771	28
22.25	.19295	.03723	3.996	67
22.58	.19577	.03833	3.938	89
23.54	.20398	.04161	3.780	100
24.17	.20936	.04383	3.683	15
24.85	.21516	.04629	3.583	15
25.28-	.21882	.04788	3.523	19
25.45	.22027	.04852	3.500	19
32.30	.27815	.07737	2.772	32

Temperature =  $+25^\circ$ 

9.16	.07985	.00638	9.655	46
9.97	.08689	.00755	8.873	49
10.65	.09280	.00861	8.308	36
15.85-	.13788	.01901	5.592	61
16.27	.14151	.02002	5.449	61
18.48	.16057	.02578	4.802	24
22.15	.19209	.03690	4.014	65
22.43	.19449	.03783	3.964	100
23.43	.20304	.04123	3.797	100
24.00	.20791	.04323	3.708	20
24.78	.21456	.04604	3.593	20
25.25	.21857	.04777	3.527	20
32.12	.27664	.07653	2.787	41

Temperature =  $+45^\circ$ 

10.05	.08759	.00767	8.802	45
11.18	.09741	.00949	7.915	81
15.78-	.13727	.01884	5.617	52
16.28	.14159	.02005	5.445	52
20.05	.17408	.03030	4.429	54
22.97	.19911	.03965	3.872	100
24.74	.21422	.04589	3.599	25
32.03	.27589	.07611	2.795	29

$2\theta$	$\sin\theta$	$\sin^2\theta$	D	Relative Intensity
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Bis(Terpyridine)Cobalt(II) Bromide Monohydrate

Temperature =  $-50^\circ$

10.98	.09567	.00915	8.059	80
15.88-	.13814	.01908	5.581	25
16.35	.14220	.02022	5.422	25
17.05	.14824	.02198	5.201	24
19.25	.16720	.02796	4.611	17
19.98	.17348	.03009	4.444	55
21.72	.18841	.03550	4.092	68
22.20	.19252	.03706	4.005	23
22.93	.19877	.03951	3.879	100
24.39	.21124	.04462	3.650	64
28.44	.24565	.06034	3.139	10
29.75	.25671	.06590	3.003	26
30.85	.26598	.07074	2.899	30
32.30	.27815	.07737	2.772	15
33.40	.28736	.08258	2.683	40
37.08	.31797	.10110	2.425	14

Temperature =  $+25^\circ$

10.95	.09541	.00910	8.081	75
15.85	.13788	.01901	5.592	36
16.27	.14151	.02002	5.449	44
17.00	.14781	.02185	5.216	19
19.15	.16634	.02767	4.635	13
19.89	.17270	.02983	4.464	51
21.63	.18764	.03521	4.109	65
22.18	.19235	.03700	4.008	27
22.82	.19783	.03914	3.897	100
24.30	.21047	.04430	3.663	65
28.38	.24514	.06009	3.145	11
29.65	.25587	.06547	3.013	25
29.94	.25831	.06673	2.985	24
30.73	.26497	.07021	2.910	26
32.18	.27715	.07681	2.782	16
33.28	.28636	.08200	2.692	38
36.85	.31606	.09990	2.439	15



$2\theta$	$\sin\theta$	$\sin^2\theta$	D	Relative Intensity
Temperature = +45°				
10.98	.09567	.00915	8.059	88
15.91	.13840	.01915	5.571	36
16.15	.14047	.01973	5.489	38
17.00	.14781	.02185	5.216	28
19.25	.16720	.02796	4.611	17
19.92	.17296	.02992	4.458	53
21.62	.18755	.03518	4.111	69
22.16	.19218	.03693	4.012	27
22.80	.19766	.03907	3.901	100
24.32	.21064	.04437	3.660	71
28.40	.24531	.06018	3.143	9
29.72	.25646	.06577	3.006	27
30.00	.25882	.06699	2.979	22
30.87	.26614	.07083	2.897	27
32.22	.27748	.07700	2.779	13
33.32	.28669	.08219	2.689	30
37.13	.31838	.10137	2.422	11

Bis(Terpyridine)Cobalt(II) Iodide Monohydrate

Temperature = -50°

10.96	.09550	.00912	8.073	35
13.53	.11780	.01388	6.545	9
16.05	.13961	.01949	5.523	31
16.35	.14220	.02022	5.422	34
16.78	.14591	.02129	5.284	43
18.33	.15928	.02537	4.841	18
19.98	.17348	.03009	4.444	41
20.88	.18121	.03284	4.255	100
22.02	.19098	.03647	4.037	22
22.85	.19808	.03924	3.892	43
24.23	.20987	.04405	3.674	56
27.73	.23963	.05742	3.217	8
28.45	.24573	.06038	3.138	10
29.11	.25131	.06316	3.068	34
29.48	.25443	.06474	3.030	39
29.55	.25502	.06504	3.023	34
29.94	.25831	.06673	2.985	15
33.20	.28569	.08162	2.699	29
35.88	.30802	.09488	2.503	22
39.95	.34161	.11670	2.257	22
40.03	.34227	.11715	2.253	21

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
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Temperature = +25°

10.96	.09550	.00912	8.073	33
13.52	.11771	.01386	6.550	12
15.94	.13865	.01923	5.561	37
16.22	.14107	.01990	5.465	37
16.84	.14643	.02144	5.265	37
18.40	.15988	.02556	4.822	10
20.02	.17382	.03021	4.436	44
20.95	.18181	.03305	4.241	100
21.98	.19064	.03634	4.044	23
22.83	.19791	.03917	3.896	45
24.22	.20979	.04401	3.675	64
27.74	.23972	.05747	3.216	12
28.39	.24522	.06013	3.144	10
29.09	.25114	.06307	3.070	40
29.50	.25460	.06482	3.028	40
29.62	.25561	.06534	3.016	30
29.93	.25823	.06668	2.986	16
33.12-	.28502	.08124	2.705	26
33.24	.28602	.08181	2.696	26
35.88	.30802	.09488	2.503	17
40.02	.34218	.11709	2.253	23

Temperature = +45°

10.94	.09532	.00909	8.088	42
13.530	.11780	.01388	6.545	14
15.980	.13900	.01932	5.547	34
16.29	.14168	.02007	5.442	36
16.82	.14626	.02139	5.272	41
18.38	.15971	.02551	4.828	11
19.97	.17339	.03006	4.447	45
20.94	.18172	.03302	4.243	100
22.02	.19098	.03647	4.037	26
22.80-	.19766	.03907	3.901	39
22.90	.19851	.03941	3.884	39
24.24	.20996	.04408	3.672	61
27.82	.24040	.05779	3.207	12
28.45	.24573	.06038	3.138	10
29.20	.25207	.06354	3.059	36
29.48	.25443	.06474	3.030	39
29.65	.25587	.06547	3.013	26
33.30	.28652	.08210	2.691	24
36.00	.30902	.09549	2.495	16
40.08	.34268	.11743	2.250	22
40.21	.34374	.11816	2.243	24

2 $\theta$	Sin $\theta$	Sin <sup>2</sup> $\theta$	D	Relative Intensity
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Bis(Terpyridine)Cobalt(II) Perchlorate Monohydrate

Temperature = -50°

8.76	.07637	.00583	10.095	9
10.94	.09532	.00909	8.088	74
16.06	.13969	.01951	5.519	29
16.70	.14522	.02109	5.309	29
17.63	.15324	.02348	5.031	9
19.40	.16849	.02839	4.576	13
20.16	.17502	.03063	4.405	58
20.29	.17614	.03103	4.377	88
21.98	.19064	.03634	4.044	11
22.96	.19903	.03961	3.874	100
24.21	.20970	.04398	3.677	58
26.55	.22962	.05273	3.358	14
29.90-	.25798	.06655	2.989	15
30.15	.26008	.06764	2.964	15
32.07	.27622	.07630	2.791	14
32.37	.27874	.07770	2.766	12
33.28	.28636	.08200	2.692	19

Temperature = +25°

8.76	.07637	.00583	10.095	11
10.88	.09480	.00899	8.133	73
15.95-	.13874	.01925	5.557	28
16.08	.13986	.01956	5.512	28
16.60	.14436	.02084	5.341	30
17.60	.15299	.02340	5.040	10
19.35	.16806	.02824	4.588	14
20.07	.17425	.03036	4.425	60
20.25	.17580	.03090	4.386	89
21.90	.18995	.03608	4.059	12
22.83	.19791	.03917	3.896	100
24.10	.20877	.04358	3.693	52
26.55	.22962	.05273	3.358	13
28.40	.24531	.06018	3.143	9
28.53	.24641	.06072	3.129	9
29.84	.25747	.06629	2.995	9
31.92	.27497	.07561	2.804	13
32.23	.27757	.07704	2.778	7
33.18	.28552	.08152	2.700	7

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
Temperature = +45°				
8.85	.07715	.00595	9.993	15
8.95	.07802	.00609	9.882	16
10.94	.09532	.00909	8.088	71
11.44	.09967	.00993	7.736	27
15.80-	.13744	.01889	5.610	35
16.07	.13978	.01954	5.516	35
16.27	.14151	.02002	5.449	36
16.73	.14548	.02116	5.300	35
17.82	.15488	.02399	4.978	13
19.48	.16918	.02862	4.557	17
20.10	.17451	.03045	4.418	71
20.42	.17726	.03142	4.350	91
22.00	.19081	.03641	4.041	16
22.92	.19868	.03948	3.881	100
24.23	.20987	.04405	3.674	45
26.88	.23243	.05402	3.317	17
28.70	.24784	.06143	3.111	10
29.98	.25865	.06690	2.981	10
32.00	.27564	.07598	2.797	17

Bis(Terpyridine)Cobalt(II) Perchlorate

Temperature -50°

8.83	.07698	.00593	10.016	26
10.32	.08994	.00809	8.573	42
10.80	.09411	.00886	8.193	80
11.60	.10106	.01021	7.629	36
11.70	.10192	.01039	7.564	38
15.83	.13770	.01896	5.599	100
16.37	.14237	.02027	5.415	79
16.74	.14556	.02119	5.297	41
17.53	.15238	.02322	5.060	40
17.83	.15497	.02402	4.975	30
19.08	.16574	.02747	4.652	26
19.98	.17348	.03009	4.444	74
20.04	.17399	.03027	4.431	74
21.50	.18652	.03479	4.134	16
22.40-	.19423	.03773	3.969	94
22.50	.19509	.03806	3.952	94
23.22	.20125	.04050	3.831	43
24.72	.21405	.04582	3.602	15
32.24	.27765	.07709	2.777	15

2 $\theta$	Sin $\theta$	Sin <sup>2</sup> $\theta$	D	Relative Intensity
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Temperature = +25°

8.78	.07654	.00586	10.073	21
10.32	.08994	.00809	8.573	37
10.77	.09385	.00881	8.215	69
11.50	.10019	.01004	7.696	33
15.85	.13788	.01901	5.592	87
19.93	.17305	.02995	4.455	83
20.00-	.17365	.03015	4.440	83
20.04	.17399	.03027	4.431	83
21.25	.18438	.03400	4.182	26
22.42	.19441	.03779	3.966	100
23.25	.20151	.04060	3.826	33
25.08-	.21712	.04714	3.551	22
25.19	.21806	.04755	3.536	22
31.85-	.27438	.07528	2.810	19
32.12	.27664	.07653	2.787	19

Temperature = +45°

8.88	.07742	.00599	9.959	23
10.00	.08716	.00760	8.846	51
10.06	.08768	.00769	8.794	51
11.22	.09776	.00956	7.887	59
15.84	.13779	.01899	5.595	73
16.07	.13978	.01954	5.516	68
16.83	.14634	.02142	5.268	43
19.88	.17262	.02980	4.467	100
21.26	.18447	.03403	4.180	31
22.37	.19398	.03763	3.975	89
22.72	.19697	.03880	3.914	40
25.08	.21712	.04714	3.551	24

# Bis(Terpyridine)Cobalt(II) Tetraphenyl Boron

Temperature = -50°

8.32	.07254	.00526	10.628	100
11.46	.09984	.00997	7.722	19
13.25	.11537	.01331	6.683	24
13.60	.11840	.01402	6.512	18
14.22	.12377	.01532	6.229	26
15.08	.13122	.01722	5.876	22
16.38	.14246	.02029	5.412	22
18.16	.15781	.02491	4.886	18



$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
18.39	.15979	.02553	4.825	18
19.12	.16608	.02758	4.642	30
19.39	.16840	.02836	4.578	34
20.94	.18172	.03302	4.243	32
21.35	.18524	.03431	4.162	28
21.63	.18764	.03521	4.109	28
21.98	.19064	.03634	4.044	40
22.61	.19603	.03843	3.933	24

Temperature = +25°

8.28	.07219	.00521	10.680	100
11.30	.09845	.00969	7.831	20
11.45	.09975	.00995	7.729	20
13.20	.11494	.01321	6.708	17
13.50	.11754	.01382	6.560	22
14.14	.12308	.01515	6.264	15
15.00	.13053	.01704	5.907	24
16.36	.14228	.02024	5.419	24
18.02	.15661	.02453	4.923	16
18.26	.15867	.02518	4.859	18
19.08	.16574	.02747	4.652	33
19.24	.16711	.02793	4.614	34
19.31	.16772	.02813	4.597	34
20.88	.18121	.03284	4.255	27
21.20	.18395	.03384	4.191	22
21.80	.18910	.03576	4.077	34
22.47	.19483	.03796	3.957	24

Temperature = +45°

8.26	.07202	.00519	10.705	100
11.36	.09897	.00980	7.790	19
13.15	.11450	.01311	6.733	19
13.46	.11719	.01373	6.579	15
14.13	.12300	.01513	6.269	20
15.00	.13053	.01704	5.907	15
15.34	.14211	.02020	5.425	23
18.07	.15704	.02466	4.910	17
18.25	.15859	.02515	4.862	17
19.03	.16531	.02733	4.664	31
19.13	.16617	.02761	4.640	31
19.25	.16720	.02796	4.611	32
20.81	.18060	.03262	4.269	27
21.19	.18387	.03381	4.193	21
21.81	.18918	.03579	4.075	32
22.45	.19466	.03789	3.961	21

$2\theta$	$\sin \theta$	$\sin^2 \theta$	D	Relative Intensity
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## Bis(Terpyridine)Cobalt(II) Sulfate Dihydrate

Temperature =  $-50^\circ$ 

8.48	.07393	.00547	10.428	25
12.04	.10488	.01100	7.352	100
14.58	.12689	.01610	6.076	58
15.92	.13848	.01918	5.568	82
16.35	.14220	.02022	5.422	92
16.93	.14721	.02167	5.238	50
19.00	.16505	.02724	4.671	19
22.80	.19766	.03907	3.901	100

Temperature =  $+25^\circ$ 

8.45	.07367	.00543	10.465	29
11.98	.10435	.01089	7.388	100
14.88	.12949	.01677	5.954	67
16.00	.13917	.01937	5.540	88
16.30	.14177	.02010	5.439	90
17.00	.14781	.02185	5.216	53
19.00	.16505	.02724	4.671	23
22.60-	.19595	.03839	3.935	97
22.85	.19808	.03924	3.892	97

Temperature =  $+45^\circ$ 

8.50	.07411	.00549	10.404	25
12.00	.10453	.01093	7.376	100
14.88	.12949	.01677	5.954	70
15.90-	.13831	.01913	5.574	78
16.27	.14151	.02002	5.449	78
16.96	.14746	.02175	5.228	44
18.98	.16488	.02718	4.676	25
22.82	.19783	.03914	3.897	100

## Bis(Terpyridine)Cobalt(II) Nitrate

Temperature =  $-50^\circ$ 

9.78	.08524	.00727	9.045	8
11.14	.09706	.00942	7.943	76
15.03	.13079	.01710	5.895	11



2 $\theta$	Sin $\theta$	Sin <sup>2</sup> $\theta$	D	Relative Intensity
15.80-	.13744	.01889	5.610	15
16.45	.14306	.02047	5.389	15
20.14	.17485	.03057	4.409	26
22.19	.19244	.03703	4.007	17
23.08	.20005	.04002	3.854	100
24.65	.21346	.04556	3.612	19
32.16	.27698	.07672	2.784	19
32.53	.28008	.07844	2.753	12
33.69	.28978	.08397	2.661	11

Temperature = +25°

9.72	.08472	.00718	9.100	9
11.06	.09637	.00929	8.001	93
14.92	.12983	.01686	5.938	12
15.80-	.13744	.01889	5.610	16
16.33	.14202	.02017	5.429	16
20.02	.17382	.03021	4.436	39
21.96	.19047	.03628	4.048	19
22.95	.19894	.03958	3.876	100
24.50	.21218	.04502	3.634	26
31.94	.27513	.07570	2.802	23
32.36	.27866	.07765	2.767	12
33.48	.28803	.08296	2.677	10

Temperature = +45°

9.78	.08524	.00727	9.045	11
11.12	.09689	.00939	7.958	86
14.98	.13035	.01699	5.915	16
15.83-	.13770	.01896	5.599	19
16.33	.14202	.02017	5.429	19
20.10	.17451	.03045	4.418	45
22.10	.19167	.03674	4.023	19
23.04	.19971	.03988	3.861	100
24.62	.21320	.04545	3.616	27
31.07	.26783	.07173	2.879	19
31.46	.27110	.07350	2.844	12
32.62	.28083	.07887	2.745	11

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## BIOGRAPHICAL SKETCH

Harold Manly Fisher was born February 19, 1940, in Fayetteville, North Carolina. He attended Fayetteville Senior High School and was graduated valedictorian in June, 1958. In May, 1962, he received the degree of Bachelor of Science with Special Attainments in Chemistry from Davidson College, Davidson, North Carolina.

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In 1962, Mr. Fisher received his commission as a Second Lieutenant in the United States Army Reserve. He was promoted to First Lieutenant in May, 1965.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 13, 1966

E. Ruffin Jones  
Dean, College of Arts and Sciences

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